

Boron Nitride Coatings

**Preparation, Characteristics
and Applications**

by
S. Marinković and Ž. Marinković

with collaboration of
H. Kötter and Ch. Meixner

GERMAN-YUGOSLAV COOPERATION
IN SCIENTIFIC RESEARCH AND TECHNOLOGICAL DEVELOPMENT

BORON NITRIDE COATINGS

PREPARATION, CHARACTERISTICS AND APPLICATIONS

by

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with collaboration of

Horst-Rainer Kötter and Dr. Christoph Meixner

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1. INTRODUCTION

Boron nitride (BN) is in many respects similar to the elementary carbon. BN exists in 4 crystalline forms of which the hexagonal, thermodynamically stable at NTP, and cubic are the best known as those similar to graphite and diamond. The third crystalline form of BN is analogous to the rhombohedral form of carbon, the fourth, BN form with hexagonal wurtzite structure being the only one without its exact carbon counterpart. Crystal structures of h-BN, c-BN and wurtzitic BN are represented in Fig. 1.1. The pressure temperature diagram of BN is presented in Fig. 1.2.

Analogy of hexagonal BN (h-BN) with graphite goes further in that, due to the similarity in bonding, h-BN has lattice parameters close to those of graphite, its main structural defects are stacking faults leading to a so called turbostratic structure, and its properties present a marked anisotropy.

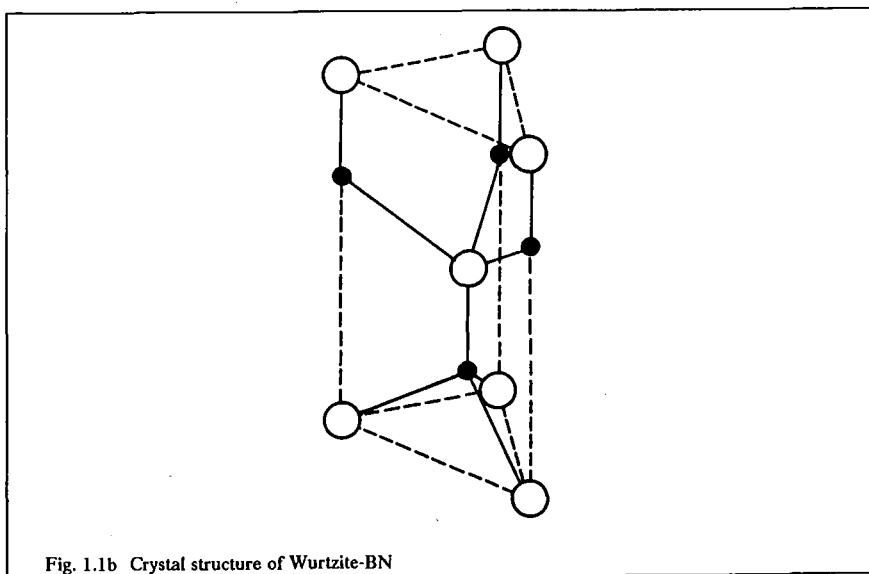
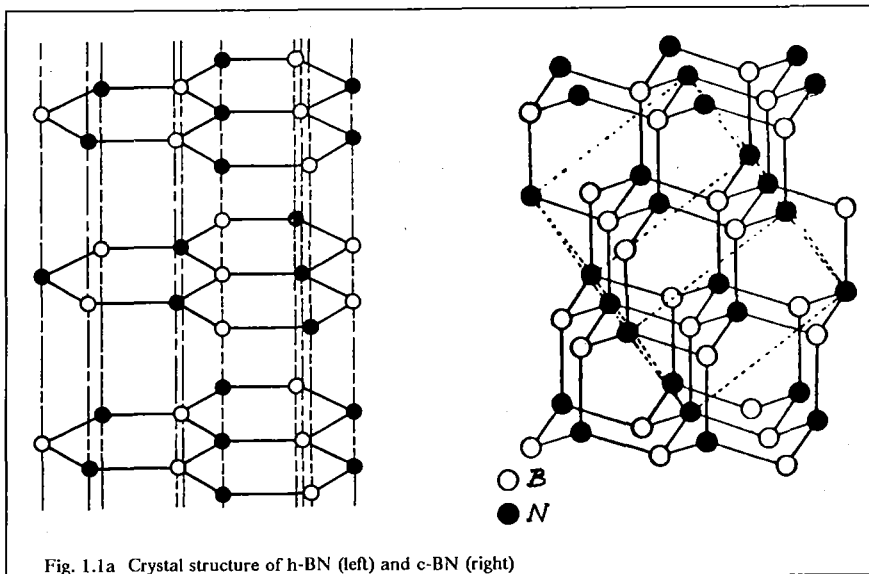
However, h-BN differs from graphite by its electronic structure: unlike graphite, in BN there are no quasi-free electrons responsible for the "semi-metallic" properties of graphite. The h-BN is therefore, unlike graphite, an excellent electrical insulator. Furthermore, h-BN does not make intercalation compounds because its electronic structure does not allow the charge transfer enabling intercalation of many molecules between the hexagonal layers in graphite.

Chemical properties of h-BN are rather similar to those of graphite, one difference being in a better oxidation resistance of h-BN.

Thus, h-BN is electrically insulating, chemically inert, thermally stable, resistant to corrosion and having desirable mechanical properties and is considered to be one of the wide-gap semiconductors. Potential and already existing applications of h-BN involve high-temperature dielectrics, heat-dissipation coatings, passivation layers, diffusion sources of B and sodium barriers. Since BN is highly transparent to X-rays, it can also be used in the fabrication of masks for X-ray lithography.

However, the very properties of BN are responsible for high prices of some BN parts produced by conventional methods, e.g. crucibles for growing single crystals of semiconductor materials. On the other hand, a number of the mentioned applications demand thin BN films.

The cubic BN has different crystal structure and properties. Thus, it is a very hard and high-friction material, as compared to the soft and lubricant h-BN. In addition, its cubic structure is intrinsically isotropic.



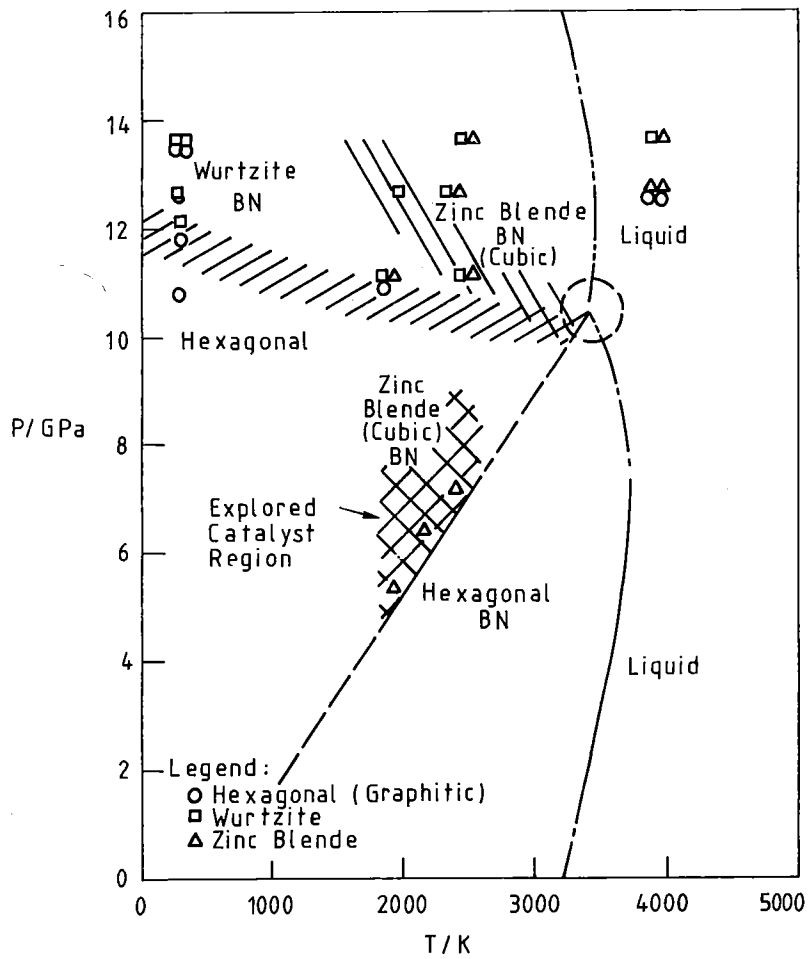


Fig. 1.2 Boron nitride pressure-temperature diagram

From what has been said stems the interest in producing the BN layers by vapour deposition methods. These methods are generally suitable for preparation of thin and thick coatings. Using volatile substances as starting materials, they are appropriate for low-cost preparation of high-melting materials, such as BN. In addition, deposition from the gas phase generally produces compact, gas impermeable materials with pronounced anisotropy, which is in the case of h-BN particularly interesting for some applications (e.g. heat shields, crucibles for crystal growth).

This study aims at presenting an up-to-date review of the recent literature covering BN preparation by both CVD and PVD methods, as well as their characteristics and existing and possible applications. During the last few years a number of papers and patents dealing with the subject appeared, showing that the interest for preparation and application of vapour deposited BN and amount of knowledge in the field are rapidly expanding. It has been thought therefore that, although there is a number of books, monographs and reviews of both CVD and PVD (Powell 1966, Gretz 1967, Jensen 1984), as well as reviews covering coatings prepared from the vapour phase (Sundgren 1986) and those dealing with more specific subjects such as plasma-assisted CVD (Thornton 1983, Kumagai 1984, Ojha 1982) or BN films (Arya 1988), an up-to-date review would be useful.

The authors are aware of the fact that they did not cover all the existing literature on the subject, but they have a reason to believe that nothing important has been missed.

As in a recent review concerning TiN coatings (Marinkovic 1988), the authors have systematized the material according to the preparation methods (CVD and reactive PVD), being conscious of the fact that the "reactive PVD" methods correspond rather to the definition of CVD.

On the other hand, a brief review of the CVD and PVD, such as presented in the mentioned TiN review, has been omitted here.

2. BORON NITRIDE PREPARED BY CHEMICAL VAPOUR DEPOSITION

In order to prepare BN by conventional CVD techniques in which the necessary energy for the chemical reactions is supplied only as heat, two different groups of volatile boron compounds have been used.

In the first group the compounds which contain boron but not nitrogen have been used, so that they must be made to react with nitrogen-containing compounds in order to produce BN. As the B-containing compound either a B-halide (BCl_3 or BF_3) or diborane have been used, the ammonium being the N-containing compound.

The second group is made of the compounds containing both elements in the stoichiometric ratio, so that BN is prepared by their thermal decomposition. The compounds used are borazine ($\text{B}_3\text{N}_3\text{H}_6$), trichloroborazine ($\text{B}_3\text{N}_3\text{H}_3\text{Cl}_3$), hexachloroborazine ($\text{B}_3\text{N}_3\text{Cl}_6$), or trimethoxyborazine ($\text{B}_3\text{N}_3\text{H}_3(\text{CH}_3\text{OH})_3$).

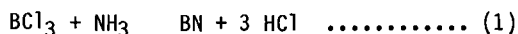
The majority of authors, of both scientific articles and patents, have used the first group compounds. In fact, the $\text{BCl}_3 + \text{NH}_3$ mixture has been most often used by the authors of patents.

In addition to the conventional CVD, the need for a lower deposition temperature and specific properties of the BN produced, have recently led to a technique which makes use of plasma to provide the energy necessary to activate the chemical reaction. In this technique, known as plasma-assisted CVD (PACVD), ionization of the gases by a d.c. or r.f. glow discharge produces electrons and ions which are accelerated in the electric field, thus increasing the number of high-energy inelastic collisions.

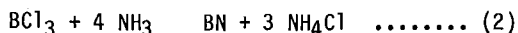
Consequently, this chapter is subdivided into the sections concerned with preparation of BN by $\text{BCl}_3 + \text{NH}_3$ (2.1), $\text{B}_2\text{H}_6 + \text{NH}_3$ (2.2), borazine and its derivatives (2.3) and the PACVD (2.4), the section 2.5 being added to include other CVD techniques used. This section contains, in addition to other gas mixtures used in the conventional CVD, other CVD techniques, namely Molecular flow CVD and Electron-enhanced CVD, the latter being considered here because of the accepted criterion according to which the decision whether a given method should be considered within CVD or PVD is mainly the apparatus used, i.e. its similarity to the CVD or PVD ones.

2.1 Preparation of BN by $\text{BCl}_3 + \text{NH}_3$ reaction

The over-all reactions



or



have been most often used. One of their advantages is that the starting compounds are inexpensive, but their disadvantage is in that the BCl_3 is a very corrosive gas, although less than the BF_3 .

Thermodynamic calculations show that the reaction should be possible (free energy becoming negative) already at about 300°C. However, as it can be seen from Table 2.1 in which a summary of the papers and patents dealing with BN deposition using the above reactions is presented, only temperatures above 700°C lead to stable BN products. The upper temperature limit used by the researchers was 2100°C.

The deposition temperature is presumably mostly dependent on the substrate to be coated. The researchers dealing with lower-melting substrates, such as carbon steel (Takahashi 1979 and 1981), fused silica, sapphire or quartz (Sano 1981, Baronian 1972, Lacrambe 1988), or copper (Motojima 1982) used temperatures not higher than 1200°C, some of them not above 700°C (Motojima 1982).

Other authors who used graphite substrates were not limited to low temperatures, except in cases where deposition of BN within the porous substrates was effected (Hannache 1983, Lacrambe 1988). In the latter case low temperature is necessary in order to make the chemical reaction (and not the diffusion) the rate-limiting step, i.e. to allow the gases to penetrate into the pores before the chemical reaction takes place. Transition temperature at which the process of BN deposition changes from surface-reaction-limited to the mass-transport-limited one was found to be 1250°C (Tanji 1987).

Other experimental conditions (total pressure, NH_3/BCl_3 ratio, other gases present) also vary in a rather broad range.

Concerning total pressure, although the complete range 0 - 1000 mbar has been covered by the reviewed papers, two main groups can be distinguished - one using ambient pressure and the other using so-called Low-pressure CVD (LPCVD) with pressures of the order of several mbar.

The majority of authors, in particular authors of the patents, have chosen LPCVD, most often combined with high temperatures (1600-2100°C)

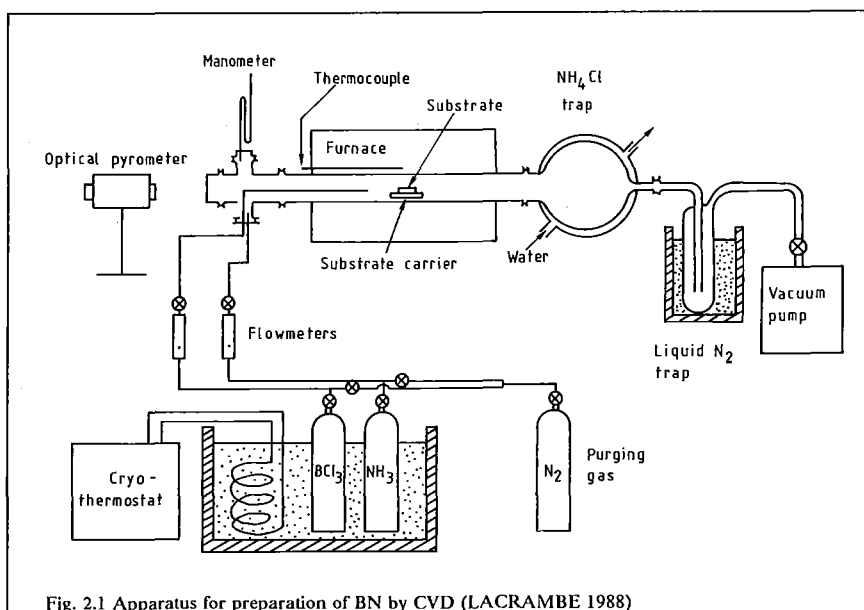


TABLE 2.1

BN coatings obtained from BCl_3 and NH_3

Preparation conditions	Apparatus, substrate	Characteristics	Applications	Reference
LPCVD without additional gas				
1450-2300°C, <65 mbar, $\alpha=1-4$. Opt.: 2000°C, ≈ 1 mbar, $\alpha=1-2$.	Graphite	For T < 1450°C glassy, unstable (sol. in water). For opt. cond.: product stable, $d > 2 \text{ g/cm}^3$, $\sigma = 180 \text{ MPa}$.	Insulating, chem. and therm. stable coatings	Basche 1964 (a)
1900°C, 1.3 mbar	Graphite	Highly oriented h-BN with high d, excel. therm. shock res., chem. stable, σ incr. with T, highest diel. strength, unusual microwave prop., IR polarizer.	Furnace components, boats, trays, tank liners, crucibles, metal evaporator parts, elec. feed-throughs, elec. insul., nozzles, coatings for graphite, heat shields, microwave IR windows and polarizers, high T	Basche (1964 (b)
1775-1800°C, 0.4 mbar, $\alpha = 2 - 5.6$	Vert., cold-wall, graphite	For $D(\text{BCl}_3) = 1.4 \text{ l/h}$ and $\alpha = 5.6$, $R = 150 \text{ } \mu\text{m/h}$; for $D(\text{BCl}_3) = 6.8 \text{ l/h}$ and $\alpha = 2$, $R = 500 \text{ } \mu\text{m/h}$.		Diefendorf 1967
1700 or 1900°C, 0.4 mbar, $\alpha = 3$: two-step procedure	Graphite mandrel	$R = 51 \text{ } \mu\text{m/h}$. 0.9 mm thick BN layer. Longer life of the crucibles.	BN crucibles for vacuum evaporation of Al	Lashway 1976
1800°C, 2.7 mbar, $\alpha = 5$	Vert., cold-wall, graphite	h-BN easily separated from graphite, cleavage parallel to substrate	BN crucibles	Malé 1979
1850-2100°C	Graphite, gases introduced through BN or graphite tube	$c \leq 0.690 \text{ nm}$, $L_c \geq 2 \text{ nm}$, $d \geq 2.1 \text{ g/cm}^3$, $MH = 620 \text{ MPa}$. With BN tube less nodules resulting in longer life of the crucible	BN crucibles for single-crystal growth	Tanji 1986 1986 (a)
1600-2000°C, 0.13 mbar, $\alpha = 4$, 9 layers deposited with T incr. of 50°C for each layer	Graphite mandrel	Highly peelable BN layers prevent vessel destruction upon removal of adherent metal	BN vessels	Iwaki 1986

1	2	3	4	5
2000°C, 13 mbar	Graphite	BN plates containing <10 ppm impurities	B dopant diffusion source for semiconductors (Si)	Kubota 1987(a)
2000°C, 13 mbar	Graphite subs., surface etched by plasma and/or H ₂ O in N ₂ at 700°C	No peeling or cracking of BN coating on cycling at 2000/20°C	No data	Kubota 1987 (b)
1900°C, 1.3 mbar, $\alpha=2$. Thin BN precoat (formed before coating) is removed together with substrate.	Graphite	Improved BN products	BN article for GaAs single crystal growth	Suzuki 1987
<1200°C, <6.5 mbar, $\alpha<1$.	Horiz., hot-wall; graphite, C-felt, silica, alumina	R rapidly incr. with T _d ; good adherence to graphite, much less to Al ₂ O ₃ ; turbostratic BN formed when HT at 1700°C transforms into h-BN; consid. abs. of O ₂ in the deposits.	Possible infiltration of BN in porous substrates	Lacrambe 1988
800-1080°C, few mbar, $\alpha=3.9$	Horiz., hot-wall	Amorph. deposit at 960°C; crystallinity incr. rapidly with HTT only if deposits are allowed to absorb O ₂ . After HT at 1700°C crystallization is fairly complete	No data	Marchand 1988
<u>LPCVD with additional gases</u>				
H ₂ + He; opt. 1680°C, 1.3 mbar, $\alpha=1.3$	Vert., hot-wall, graphite	R=400 μ m/h; anis. BN, white, regular. At high T reacts with Ti, Ta, W.	Insulator for elec. tubes up to 800°C	Clerc 1975
H ₂ ; 1000-1600°C, 1-100 mbar, $\alpha^2=3$	Vert., cold-wall; 2-D carbon/carbon (ex-PAN fabric densified by little PC). $P_0=45\%$	For T _d = 1000-1300°C achieved infiltration - amorph. BN; for T _d =1300-1600°C cryst., but only on surface (no deposition).	Carbon/carbon/BN composite. Improved oxid. resistance.	Hannache 1983
N ₂ ; 1875°C, 0.65 mbar	Graphite mold	The crucible stood 25 cycles of melting 1300°C and ultrasonic removal of B ₂ O ₃ with initial peeling thickness 25 μ m.	1 mm thick BN crucible for Czochralski growth of comp. semiconductor.	Kawasaki 1986 (a,b)

1	2	3	4	5
N ₂ ; 1900-1970°C, 1 mbar	Graphite	0.1-5 mm thick BN layer contg. ≤ 0.1% C and almost no C or B ₄ C particles > 5 μm diam. ρ ≥ 3 × 10 ⁸ ohm cm.	Liner for crucibles for growing single crystals of GaAs	Tanji 1986 (b)
N ₂ ; 900-1900°C, 2.7 mbar, α ₂ =4	Vert., hot-wall; graphite	For T _d < 1250°C glassy, isotr., for T _d > 1250°C highly oriented	Components for LEC, HB, MBE crystal semiconductor growth	Tanji 1987
As in the foregoing article	As foregoing	Low-crystallinity BN - catastrophic failure; higher crystallinity - stable delamination.	Crucibles for LEC	Iwasa 1987
H ₂ ; 2 layers: at 800 and 1500°C; 1.3 mbar.	Graphite crucible	5 μm thick intermediate BN film with random orientation and CTE = 4 × 10 ⁻⁶ °C ⁻¹ and 150 μm thick BN coating. No peeling of the crucible.	Crucible for vacuum deposition of Al.	Yamaguchi 1987
N ₂ ; >1900°C, <26 mbar <u>CVD at medium pressure</u>	Graphite mold	R < 300 μm/h; c < 0.680 nm.	Crucibles for semiconductor growth	Kawasaki 1987
N ₂ or He; 1100-1600°C, 0.2-650 mbar	Cold-wall	Up to 200-260 mbar, R ≈ 1 mm/h, then decr. At T _d = 1100-1350°C, R = 0.6 mm/h, then incr. exponentially to 1.5 mm/h. Subs. and carrier gas do not affect deposition process and BN structure. Turbostratic BN, c = 0.688 nm, P ₀ = 0.5-2.5%, d = 1.45-1.55 g/cm ³ , MH = 400-600 MPa. For T _d > 1550°C, h-BN.		Liepin 1974
H ₂ ; 1200-2000°C, 6.5-80 mbar, α = 0.64	Cold-wall, Joule effect, graphite	For T _d = 1200-2000°C and 13-80 mbar - turbostratic BN; for T _d > 1700°C and 6.5 mbar - h-BN and turbostratic BN	High-temperature crucibles, jigs, insulators	Matsuda 1986
No carrier gas; 2000°C, 130 mbar, α = 2	Graphite container	BN coating: inside R = 120 μm/h, d = 2 g/cm ³ ; outside R = 160 μm/h, d = 1.2 g/cm ³ .		Kubota 1986

1	2	3	4	5
<u>CVD at atmospheric pressure</u>				
No carrier gas; 600-900°C, $\alpha = 2$	Quartz on graphite susceptor	R=0.3 $\mu\text{m/h}$; $L_c=3$ nm; $E_g=5.83$ eV, refractive index 1.9-2.0		Baronian 1972
H ₂ + Ar; 900-1200°C, $\alpha \geq 6$	Carbon steel	R=40-50 $\mu\text{m/h}$; For $T_d < 1100^\circ\text{C}$ - semi-crystalline BN, $c=0.70$ nm; for $T_d > 1100^\circ\text{C}$ - crystalline h-BN, $c=0.666$ nm. Fe and Ni (from subs.) and H ₂ favorize crystallinity	Can be used in high-T molten salt or corrosive gas environment	Takahashi 1979
H ₂ + Ar; 900-1200°C, $\alpha = 5$	Cold-wall, vert.; carbon steel	Stoichiometric BN film; for $T_d=900$ -1000°C amorph., for $T_d=1200^\circ\text{C}$ cryst. R=40 $\mu\text{m/h}$ at 1200°C. Transmittance 20-40 % in visible, decr. in UV (1% at 250 nm)		Takahashi 1981
Ar; 600-1100°C, $\alpha \geq 100$	Fused silica, sapphire	For $T_d < 900^\circ\text{C}$ white, opaque, non-adherent BN films; Above 1000°C colorless, transparent, well-adherent chem. inert films. R 1 $\mu\text{m/h}$ on sapphire and 0.5 $\mu\text{m/h}$ on fused SiO ₂	Masking, passivation	Sano 1981
H ₂ + Ar; 250-700°C, $\alpha = 1-6$	Vert., hot-wall; Cu-plate	Transparent films; For $T_d < 450^\circ\text{C}$ lose 20-30%, for $T_d > 600^\circ\text{C}$ very stable, lose 1-2% at temperatures below 750°C. R=3 μm at 500, 17 $\mu\text{m/h}$ at 700°C		Motojima 1982
<u>CVD at unreported pressure</u>				
No data	Graphite former coated with BN powder and heated	The deposited BN is separated from graphite without defect formation. The graphite former can be used up to 15 times and BN crucibles have high thermal shock resistance.	BN crucibles	Tanaka 1985
H ₂ ; 1800°C	Graphite plate ground with emery paper	A 50 μm thick BN coating is air-impermeable, has excellent adhesion and extended life	Crucibles, heaters	Hara 1985

1	2	3	4	5
H ₂ ; 2000°C	Graphite coated with B-N-Ti ternary ceramics	0.1 mm thick BN coating has very good adhesion to substrate		Nakae 1985
No carrier gas	Rotated graphite	NH ₃ and BCl ₃ (or BF ₃) are introduced into reactor using separate pipes		Kawai 1986
No carrier gas; 1950°C	Graphite mold	R=72.3 μm/h; A BN layer 1 mm thick has MH < 620 MPa (load parallel to laminar structure)	BN crucible for growth of compound semiconductors	Watanabe 1987
H ₂ .	ZrB ₂ , TiB ₂ , TiN, TiC or graphite	A 10-100 μm layer of BN has d=2 g/cm ³ Longer life of the nozzles.	Nozzles for coating Al on glass fibres.	Segawa 1988
No carrier gas.	Graphite	Multilayer BN structure with extended life	BN crucibles for metal vapour deposition	Watanabe 1988
No carrier gas; ≤ 1600°C	Graphite	50 μm thick BN coating. No peeling of the coating or cracking after 10 cycles 400/20°C.	Crucibles, boats	Aiba 1988

Designations: CTE = coefficient of thermal expansion; d = density; E_g = optical edge; HB = horizontal Bridgman; HT = heat treatment; IR = infrared; LEC = liquid encapsulation Czochralski; MBE = molecular beam epitaxy; MH = microhardness; P_o = open porosity; PC = pyrolytic carbon; R = deposition rate; σ = breaking strength; T = temperature; T_d = deposition temperature; UV = ultraviolet

Abbreviations: abs. = absorption; amorph. = amorphous; anis. = anisotropic; chem. = chemical(ly); compd. = compound; cond. = condition(s); consid. = considerable; contg. = containing; cryst. = crystalline; diam. = diametre; decr. = decrease; diel. = dielectric; elec. = electric(al); excel. = excellent; horiz. = horizontal; incr. = increase; insul. = insulator; isotr. = isotropic; opt. = optimum; oxid. = oxidation; res. = resistance; sol. = soluble; subs. = substrate; therm. = thermal(ly); vert. = vertical

(see Table 2.1). An experimental apparatus for LPCVD of BN is represented in Fig. 2.1.

2.1.1 Influence of deposition conditions on deposition rate and boron yield

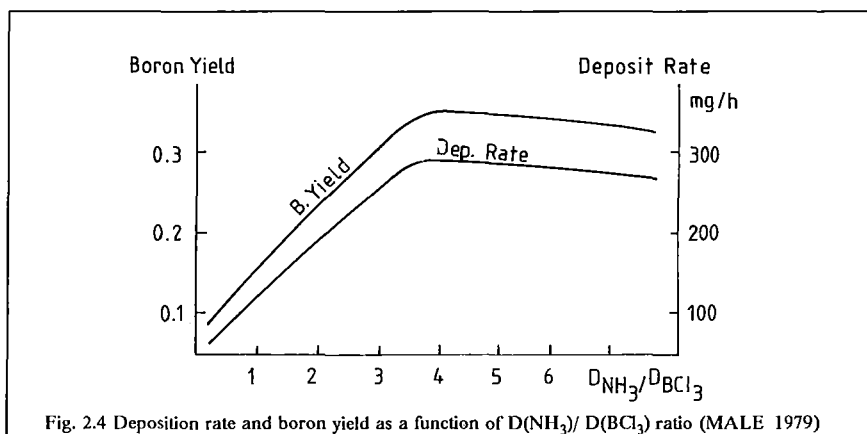
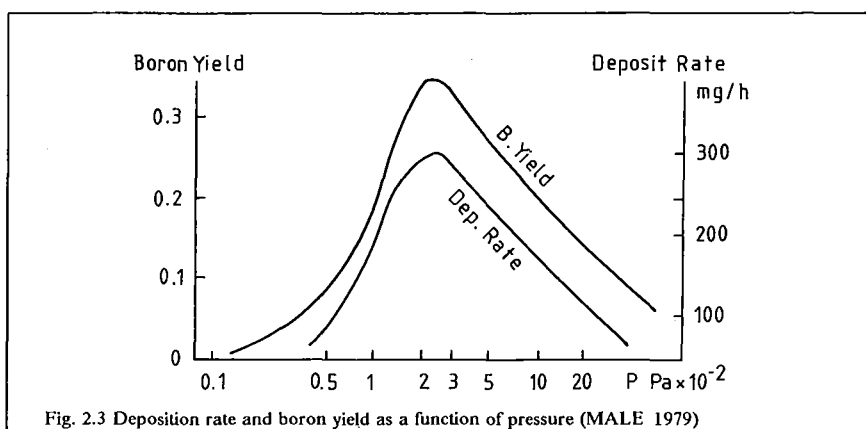
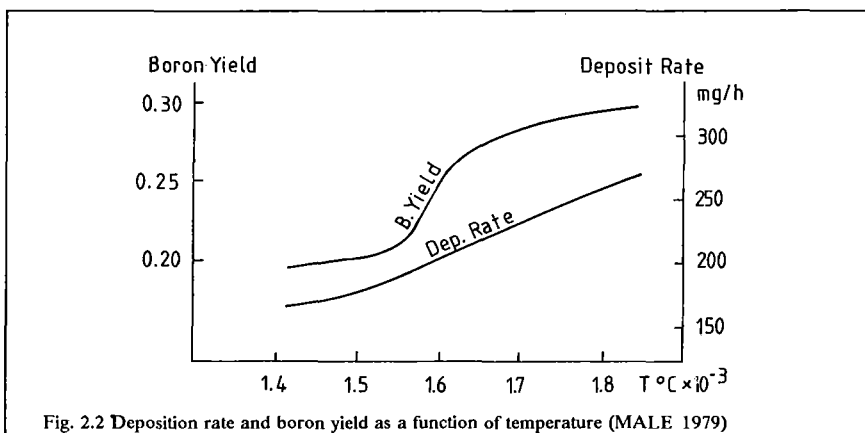
The papers and patents concerning deposition of BN usually do not give a detailed description of the apparatus and working conditions used and therefore the statements presented here must be taken with reserve. Furthermore, the information in the available literature is obtained almost exclusively from the laboratory experiments with limited dimensions of the apparatus and, in particular, with small dimensions of substrates, so that almost no data relative to deposit thickness distribution exist. It seems, however, that one of the problems which deserves particular attention is to reach a uniform thickness distribution of BN along the substrate.

The position of the tubes used to introduce the BCl_3 and NH_3 with respect to the substrate plays an important role. From the data presented in the papers it follows that the NH_3 -tube is more often brought closer to the substrate, although an equal distance of both tubes has also been used and in one case (Takahashi 1979) the BCl_3 tube is reported to have been closer. Coaxial tubes are often used.

The tube closer to the substrate should not be too distant from it because otherwise the reaction between the gases will occur prematurely and no or little deposit will be obtained on the substrate. This distance has been usually a couple of centimeters, although the distance of 9 cm has also been reported (Clerc 1975). The other tube (more distant from the substrate) was most often close to the first one, but it could also be at the very entrance of the reactor (Sano 1981).

Influence of working conditions (deposition temperature, T_d , from 1450 to 1800°C, pressure, P , from 0.13 to 40 mbar, BCl_3 flow-rate, $D(\text{BCl}_3)$, from 0.1 to 2 l/h, NH_3 flow-rate, $D(\text{NH}_3)$, from 0.3 to 0.6 l/h) on the deposition rate and yield of boron (ratio of boron mass in the deposit calculated supposing that the deposit has a stoichiometric composition, to boron mass contained in the consumed BCl_3) has been systematically studied by Malé (1979) (Fig. 2.2). Both the deposition rate and B yield were found to increase with T_d , the B yield showing a sudden increase between 1550 and 1650 °C, becoming much less dependent on temperature above 1650°C.

Influence of P , studied at 1700°C, shows a distinct maxima at 2.7 mbar,



the deposition rate decreasing by a factor of about 6 at about 50 mbar (Fig. 2.3).

Both the deposition rate and B yield were found to increase with NH_3/BCl_3 ratio, α , up to α value of 3.8 and to remain unchanged above it (Fig. 2.4). This result differs from that obtained by Motojima (1982) who found a rather distinct maximum of deposition rate for $\alpha \approx 1.5$ at $T_d = 700^\circ\text{C}$. The deposition rate and B yield were also found to depend on $D(\text{BCl}_3)$: other parameters being kept at optimum values, the deposition rate increased monotonously with $D(\text{BCl}_3)$ but B yield presented a maximum for a rather low $D(\text{BCl}_3)$ value.

An increase of deposition rate with T_d was also found by other researchers (Motojima 1982, Tanji 1987, Yamaguchi 1987).

From the Arrhenius plot of the deposition rate (Fig. 2.5) giving 209 kJ/mol as the activation energy in the lower T_d region (below 1250°C) and showing much less temperature dependent deposition rate at higher T_d , Tanji (1987) concluded that the surface reaction is the rate-limiting process below 1250°C and the mass transport controls the process above this temperature. The authors have found that deposition rate exponentially decreases with the distance along the gas flow at 1900°C (at lower T_d there is a considerable deviation from the exponential relationship), but that the slope of the log (deposition rate) vs. distance straight lines decreases (i.e. the distribution becomes more uniform) as the gas flow-rate is increased.

Another interesting result of the authors is that deposition rate is proportional to the BCl_3 concentration in the 4-20 Pa partial pressure region, but it is independent on the NH_3 concentration. The results can be explained by the boundary layer model, the BCl_3 being the rate-limiting species in the lower BCl_3 concentration region.

Concerning the absolute values of the deposition rate obtained by different authors, it may be interesting to note that analysis of a number of patents regarding BN deposition from BCl_3/NH_3 mixture (with or without other gases) shows that only in several of them the values of the deposition rate are given (Yamaguchi 1987, Kawasaki 1987, Watanabe 1987, Kubota 1986, Lashway 1976, Diefendorf 1967). Except in two cases (Yamaguchi 1987, Diefendorf 1967), all of them are obtained with T_d between 1900 and 2000°C . The values obtained for this T_d interval vary between 72 and $500 \mu\text{m/h}$, the more recent ones (obtained in 1986-1987) covering the range from 72 to $<300 \mu\text{m/h}$, which can be compared with max. $200 \mu\text{m/h}$ obtained by Tanji (1987) in laboratory experiments.

The NH_3/BCl_3 ratio (α) is a rather important parameter. Majority of researchers have used the values greater than unity (excess ammonia), although

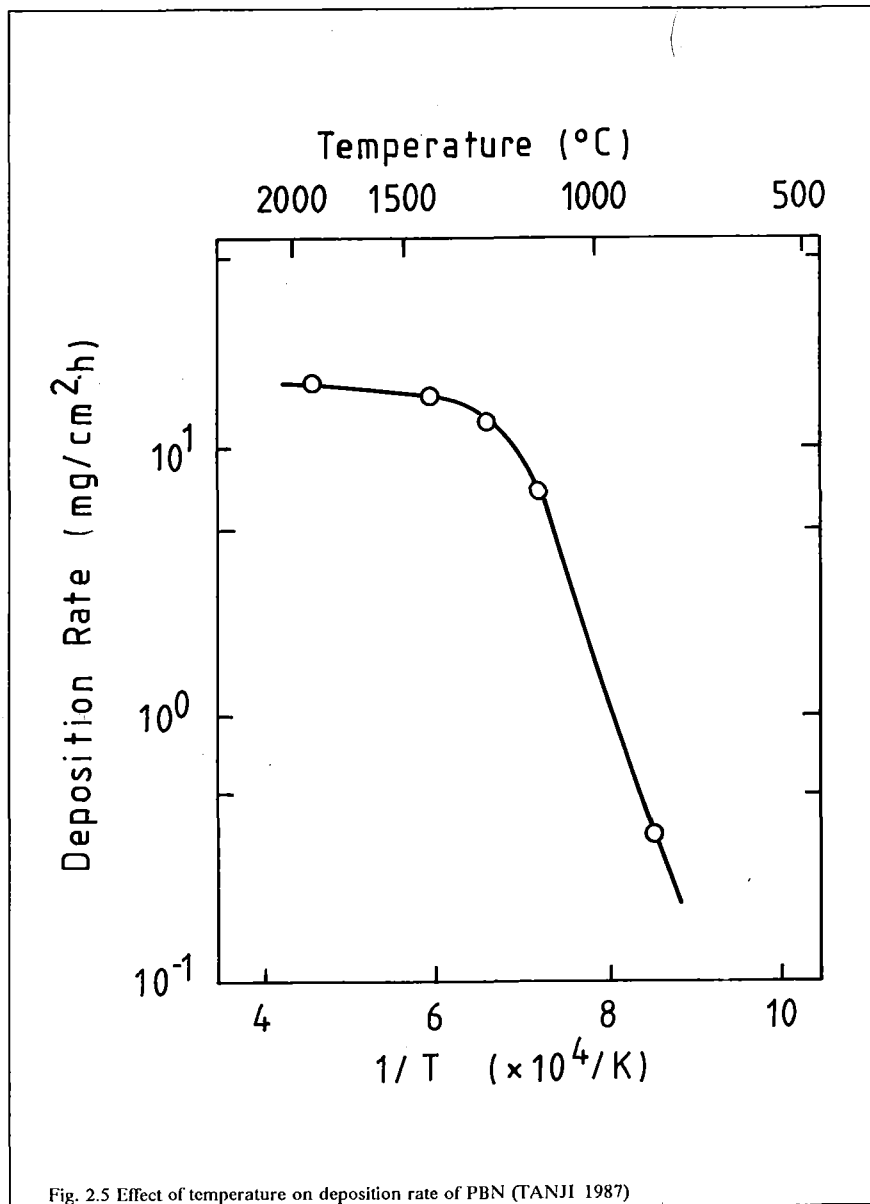


Fig. 2.5 Effect of temperature on deposition rate of PBN (TANJI 1987)

the ratios less than unity have also been reported (Matsuda 1986). In fact, the reaction (1) requires $\text{NH}_3/\text{BCl}_3 = 1$, while for the reaction (2) a ratio of 4 is necessary. The values less than unity imply that not all of the BCl_3 will react. However, although the eqs. (1) and (2) imply that for all values equal or greater than unity BCl_3 should be completely consumed, the exact value of the ratio determining only nature and relative amount of the by-products (i.e. HCl , NH_4Cl , or their mixture), certain experimental results indicate that it is not so (Malé 1979).

Many authors have used one or more additional gases (H_2 , N_2 , Ar, He) mainly to carry (and/or dilute) the BCl_3 vapour. According to Hannache (1983) who studied thermodynamical aspects of the CVD procedures involving $\text{BCl}_3 + \text{NH}_3 (+\text{H}_2)$ mixtures, addition of hydrogen may have the (undesirable) effect of producing elementary boron, which is not produced if the initial gas mixtures without hydrogen are used.

Generally the advantage of using additional gas can be in the following:

- a) To carry the boron compound vapour;
- b) To make a more uniform distribution of the carried boron compound in the reaction zone (by diluting it with a larger volume of the carrier gas);
- c) To permit to achieve wider range of flow-rate, i.e. of residence time.

The apparatus used has been either vertical or horizontal. In the vertical arrangement the gases are most often introduced in the bottom, but gas inlet on the top of the reaction chamber has also been used. In all cases the main gas components (NH_3 and BCl_3) have been introduced separately and allowed to mix only in the vicinity of the substrate. Coaxial arrangement of the gas inlet tubes has often been designed, usually with the central tube for NH_3 closer to the substrate. In general, NH_3 is most often brought more closely to the substrate (Clerc 1975, Matsuda 1986, Sano 1981), although the arrangements with BCl_3 being brought closer to (Takahashi 1979 and 1981), or with both gases at equal distance from the substrate (Hannache 1983) have also been reported.

Concerning the mode of heating, it could be either resistance, induction, or by Joule effect. Induction heating has the advantage that only substrate is heated directly, the reactor walls remaining cool. The same applies to the heating by Joule effect, but the need for high current may present technical problems.

2.1.2 Influence of deposition conditions on BN coating properties

A broad range of deposition conditions used by different authors had as a consequence a variety of properties of the deposited BN.

Stoichiometry

The chemical composition of the samples has not often been reported by the researchers dealing with CVD of BN.

It has been reported that BCl_3 and NH_3 readily react already at room temperature to form a white powder with composition $\text{B/N/Cl} = 1/4/3$ (atom ratio). It is thought that the powder is probably composed of boron amide compounds, boron imide compounds and NH_4Cl (Matsuda 1986). Chemical composition of the coatings formed at low temperatures (several hundred degrees) is still different from that of BN. Only the coatings deposited at or above 700°C are thermally and chemically stable, their behaviour corresponding to that of h-BN (Motojima 1982). Such a behaviour is the reason why NH_3 and BCl_3 have to be introduced separately into the CVD reactor and why their reaction should be made to take place in the hot zone near the substrate.

According to Marchand (1988), the B/N ratio of the samples prepared at $800\text{--}1080^\circ\text{C}$ with $\alpha \approx 4$ is always greater than unity (between 1.03 and 1.20).

The same authors found that BN prepared at $960\text{--}1080^\circ\text{C}$ had a strong tendency to absorb oxygen (up to 24 atomic %), while after HT at 1700°C it absorbed only a slight amount of oxygen.

The conditions of the CVD process, in particular the NH_3/BCl_3 ratio (α) and presence of hydrogen in the initial gas mixture, determine whether the deposit will contain phases other than BN. It follows from thermodynamic calculations (Hannache 1983) that the deposit should contain free B in addition to BN only when excess H_2 is present in the original gas mixture and for $\alpha > 1$, which is verified experimentally for α values considerably lower than unity. If there is no hydrogen in the initial mixture (i.e. $\text{NH}_3 + \text{BCl}_3$ system), the deposit does not contain free B, which is also verified experimentally. The deposits without free B seem to be considered to be stoichiometric BN, which needs experimental confirmation (see also Marchand 1988).

Crystal structure

The coatings produced by the CVD method have more or less defective structure, but in no case structure other than hexagonal has been reported. As the deposition temperature increases, coatings become more crystalline. At low deposition temperatures they are amorphous, and with increasing temperature first turbostratic and then more crystalline hexagonal coatings are produced. Although for the amorphous coatings it cannot be said with

certainty that they have a short range order corresponding to the h-BN, their properties point to such a conclusion. Thus, IR spectra of the amorphous BN are similar to those of the crystalline samples (Motojima 1982), and if the former are heat-treated, they become crystalline with (turbostratic) hexagonal structure. This behaviour is similar to that of carbon, although BN shows more rapid increase of crystallinity with increasing heat treatment temperature (Marchand 1988). The amorphous BN is considered therefore to correspond to a kind of hexagonal turbostratic structure (Takahashi 1981).

Total pressure also influences structure of the deposits, lower pressure leading to an increased crystallinity (Matsuda 1986). According to Takahashi (1979), crystallinity of the coatings increases with increasing partial pressure of hydrogen in the initial gas mixture.

The better crystallized coatings are anisotropic, their layer planes being parallel to the substrate surface.

According to Marchand (1988), heat treatment of BN deposits prepared at 960-1080°C leads to their crystallization similar to graphitization of pyrolytic carbon. The crystallization proceeds much more readily if the deposits are allowed to absorb oxygen after the deposition, i.e. before heat treatment. A considerable amount of absorbed oxygen (up to 24 atomic %) acting as a "graphitization" catalyst, leads to a fairly complete crystallization of BN by HT at 1700°C, while the same BN sample not allowed to absorb oxygen showed a very little effect of HT on crystallization under identical conditions (Fig. 2.6 a, b).

Microstructure

A pebble-like structure is usually observed on the deposition surface. Matsuda (1986) found, however, that the surface structure of a crystalline deposit was composed of pyramidal pentagonal facets. The growth texture, as seen in polarized light on the BN layer cross-section, is composed of many cones with their size increasing as the reaction proceeds (see e.g. Belforti 1961).

A catalytical action of the iron-group elements is observed in nucleation of BN deposits. Thus, Fe grains in a carbon steel substrate promote formation of the first BN layer, leading to "nodular" texture (Takahashi 1979).

Adherence

Although adherence of the coatings to the substrate depends on the substrate material and deposition conditions, it was found to be generally satisfac-

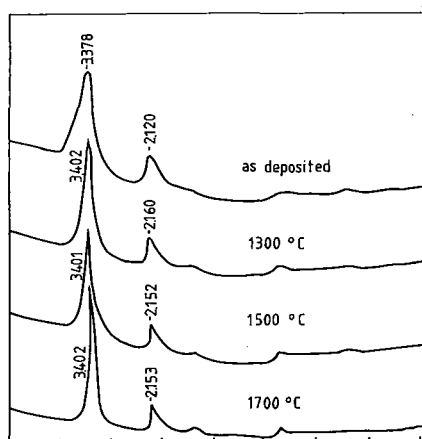


Fig. 2.6a X-ray diffractograms of BN samples heat-treated before exposure to air (MARCHAND 1988)

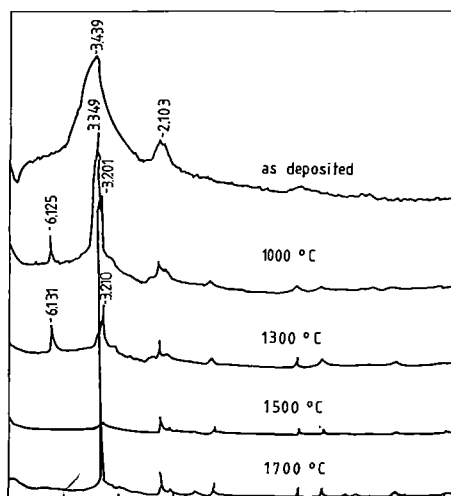


Fig. 2.6b X-ray diffractograms of BN samples heat-treated after exposure to air (MARCHAND 1988)

tory. The adherence was found to be good to graphite and much less to Al_2O_3 (Lacrambe 1988). A 50 μm thick BN coating on graphite deposited at $T_d \leq 1600^\circ\text{C}$ did not show any peeling or cracking after 10 cycles of heating to 400°C and quenching in water at 20°C (Aiba 1988).

Kubota (1987) found that BN film on graphite is more stable if the graphite substrate is treated by plasma and/or reactive gas (water vapour) prior to deposition. Excellent adhesion of a 50 μm thick BN coating to graphite, as well as absence of pores resulting in air impermeability and an extended life of the BN-coated graphite parts were achieved by grinding graphite surface with emery paper prior to BN deposition (Hara 1985).

Other procedures used to prevent peeling of BN coatings and increase their adhesion to the graphite substrate make use of an intermediate layer. Thus, a 5 μm thick BN film having random orientation and then a 150 μm anisotropic BN layer were deposited at 800 and 1500°C , respectively (Yamaguchi 1987). A B-N-Ti intermediate coating and a BN coating had a very good adhesion (Nakae 1985).

Good adhesion is not always desirable because of the stresses developed during cooling immediately following the deposition. Thus, a recent analysis of the stresses in a PBN crucible (Naito 1988) reveals that radial tension and combined tangential tension and compression exist, the maximum stresses increasing with increasing crucible thickness. A negative effective thermal expansion coefficient may result in the tangential direction. The radial tensile stress which enhances delamination increases due to the PBN attachment to the graphite mandrel. Therefore, when PBN crucibles were prepared by depositing BN on graphite mandrels and separating thus obtained BN crucibles from graphite, the adhesion was lessened either by using an intermediate well-adherent thin BN layer which was separated together with graphite from the BN article (Suzuki 1987), or by coating the graphite mandrel with BN powder prior to deposition of the BN layer (Tanaka 1985). In both cases the PBN articles have better properties, and the graphite mandrel in Tanaka's procedure could be repeatedly used up to 15 times.

Mechanical properties

Bending strength of PBN across the BN layers (which corresponds approximately to the tensile strength in the direction parallel to the layers) is about 105 MPa at room temperature (Basche 1964). The strength increases with increasing temperature up to 2200°C , which is also a behaviour typical of carbon materials.

The CVD BN coatings, both amorphous and with a developed hexagonal structure, do not have high hardness and this property is apparently seldom

measured. A value of <620 MPa is given by Watanabe (1987) for a BN micro-hardness obtained in the direction parallel to the laminar structure of the deposit.

Optical properties

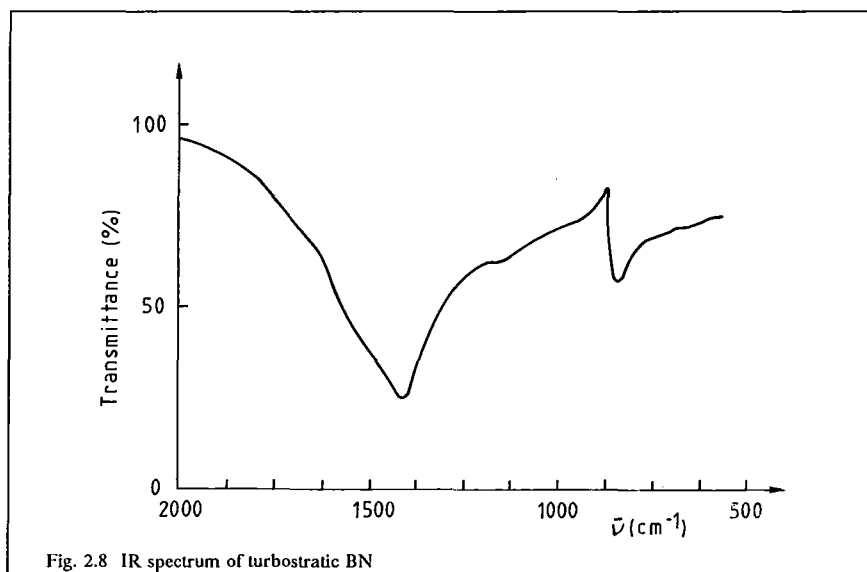
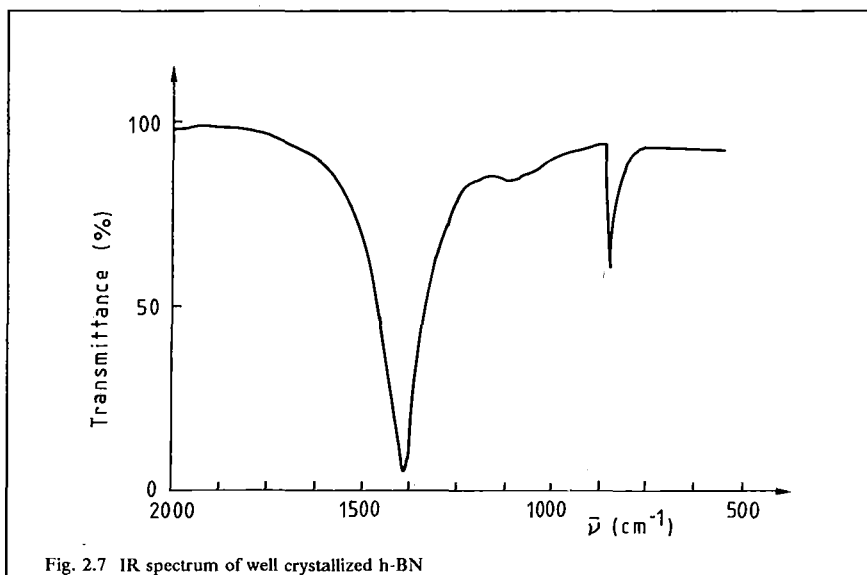
The infrared (IR) transmission spectrum of BN consists of two absorption bands: a strong in-plane B-N stretch absorption band at about 1400 cm^{-1} and a weaker out-of-plane one at about 800 cm^{-1} (Geick 1966). The exact location of the weaker band is thought to be related to the degree of alignment between the flat B_3N_3 hexagonal layers. IR spectra of a well-crystallized h-BN and turbostratic BN are shown in Fig. 2.7 and Fig. 2.8, respectively.

In the spectral range from 1000 to 2000 nm there is a sharp absorption edge in the near ultraviolet (UV). Its location is at 5.8-5.9 eV (214-210 nm) and the main absorption peak is located at 6.2 eV (200 nm) (Baronian 1972, Sano 1981, Zunger 1976).

The appearance of the CVD BN coatings varies from colourless transparent to white opaque. According to Takahashi (1979, 1981), who used a deposition temperature in the 900-1200°C range, there is a correlation between transparency of the films and their crystallinity, the crystalline films being transparent and semicrystalline films being white-coloured opaque. Both crystallinity and transparency increase with increasing deposition temperature. The authors found that (poly)crystalline BN films 55 μm thick had a light transmittance of about 40 % in the IR and visible regions (except for the absorption bands in the IR), but it decreased in the UV down to 1 %. Colourless transparent films were also obtained by Sano (1981) at substrate temperature above 1000°C, while at temperatures below 900°C white opaque films were obtained. However, Matsuda (1986) who, unlike the previous authors prepared BN coatings at a reduced pressure, found that transparent layers were formed at lower deposition temperatures (below 1400°C) and higher total pressures (above 26 mbar), while opaque films were obtained at higher temperatures and lower pressures.

According to Motojima (1982), the NH_3/BCl_3 ratio also influences the appearance of the films. Transparent or slightly opaque films were obtained at temperatures higher than 300°C and for α values between 1 and 6, while for a large excess of NH_3 ($\alpha > 6$), or at temperatures below 300°C white powders were obtained.

Moore (1969) reported that compression annealing of CVD BN at temperatures above 2300°C produced a transparent, highly oriented crystalline BN of theoretical density.



Refractive index of the BN films was found to be 1.65 (Takahashi 1981), which is considered by the authors to be the intrinsic value of the BN film (supposed to have a stoichiometric composition). However, Baronian (1972) found values ranging from 1.9 to 2.0.

Reflectivity spectrum of thin BN films deposited at 600-900°C measured in the region 220-320 nm shows a maximum of about 20 % near 230 nm, after which the reflection coefficient gradually decreases to below 10 % (Zunger 1976).

According to Moore (1969), cleaved surfaces of a highly oriented CVD BN obtained by compression annealing above 2300°C exhibit high reflectivity.

Thermal properties

Unlike pyrolytic carbon, thermal conductivity of PBN in the direction perpendicular to the layers increases with temperature linearly from 0.0146 at 0°C to 0.029 W cm⁻¹ °C⁻¹ at 800°C. Thermal conductivity parallel to the layers is 0.63 W cm⁻¹ °C⁻¹ and independent on temperature at least up to 430°C (Basche 1964 b). Large anisotropy of thermal conductivity (ratio of almost 50 in the two directions) is analogous to pyrolytic carbon.

Thermal expansion coefficient also shows large anisotropy, being close to zero in the direction parallel to the BN layers and 36.5 x 10⁻⁶°C⁻¹ perpendicular to the layers (Fig. 2.9, Basche 1964 b).

The PBN has excellent thermal shock resistance (Basche 1964, Aiba 1988).

Electrical properties

Electrical conductivity of the crystalline PBN film prepared at 1200°C was found to range from 4.7 x 10⁻¹³ Sm⁻¹ at room temperature to 1.6 x 10⁻⁹ Sm⁻¹ at 200°C (Takahashi 1981). The film deposited at 1920°C containing 0.01% C was found to have electrical conductivity of 3.3 x 10⁻⁷ Sm⁻¹ (3 x 10⁸ ohm cm resistivity, Tanji 1986 b).

The dielectric strength of PBN is higher than that of any other material available. A breakdown value of 157000 V/mm was obtained at room temperature in the direction perpendicular to the layers (Basche 1964 b).

Thus, the PBN has an extremely high electrical resistivity and good thermal conductivity (parallel to the layers), which is a quite unusual combination found only in one other material, beryllium oxide.

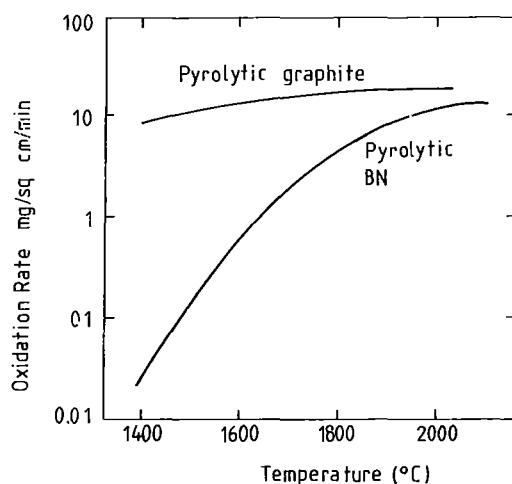


Fig. 2.9 Thermal expansion of BN and pyrolytic carbon parallel (a-direction) and perpendicular to the layers (c-direction) (BASCHE 1964b)

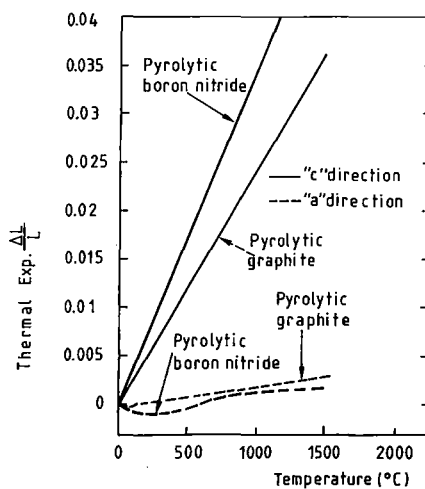


Fig. 2.10 Oxidation resistance of BN and pyrolytic carbon (BASCHE 1964b)

Chemical properties

Stability of the films. Transparent films deposited at low temperature (below 450°C) are reported to be unstable in a moist atmosphere, gradually devitrifying from the surface to the bulk by forming fissures (Motojima 1982). The degree of the instability increased as the deposition temperature decreased. The films swelled and were partly dissolved in water. By heating above 600°C in an inert atmosphere a weight loss of 20-30 % was observed. The films deposited above 600°C were stable, neither swelling nor decrease in their transparency was observed, and heating above 600°C led to a weight loss of only 1-2 %.

The films obtained at 1200°C at ambient pressure are reported to be stable at least up to 900°C (Takahashi 1981). A small decrease in weight which is virtually completed up to 400°C is ascribed to the desorption of water or weakly bonded hydrogen from the surface of the film. No thermal effects were found by the DTA.

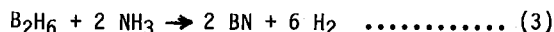
Oxidation stability of the coatings increased with increasing temperature of their deposition. For the films deposited at 700°C the temperature at which their oxidation begins was found to be about 750°C (Motojima 1982).

Oxidation resistance of PBN is considerably higher than that of pyrolytic carbon at temperatures below 2000°C (Fig. 2.10, Basche 1964 b). The activation energies obtained from the oxidation rates in air-flow for pyrolytic carbon and PBN were 14.3 and 87.7 kJ/mol, respectively (Basche 1964 b). Oxidation resistance was found to increase with increasing deposition temperature. For the films deposited at 700°C oxidation begins about 750°C (Motojima 1982).

The coatings deposited between 600 and 1100°C are chemically inert even to nitric and hydrofluoric acids at room temperature (Sano 1981).

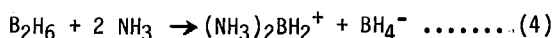
2.2 Preparation of BN coatings by B₂H₆ + NH₃ reaction

The overall reaction is



As a reagent for the CVD process, B₂H₆ has the advantage of having a favourable free energy change for the above reaction. It amounts to -690 and -740 kJ/mol at 630 and 830°C, respectively, offering the hope that the reaction will be complete at relatively low temperatures (Rand 1968).

The reaction occurs in separable steps (Adams 1964): at room temperature there is immediate formation of a stable white solid borohydride, the diammoniate of diborane



which at or above 200°C rearranges to the ring compound B₃N₃H₆ (borazine) and some polymeric material, (BNH₂)_n. Stronger heating drives off the hydrogen progressively, forming polymeric (BNH)_n and finally BN.

A disadvantage of B₂H₆ is that it requires refrigerated storage at a temperature below -20°C to prevent its decomposition.

The B₂H₆ + NH₃ mixture (usually with addition of H₂ or N₂) was mostly used to deposit BN at low temperatures, i.e. from 250 to 1250°C (Rand 1968, Hirayama 1975, Shohno 1979, Murarka 1979, Adams 1980) with silicon (wafers) as a substrate material (Table 2.2). Only Rand (1968) used, in addition to Si, other substrates such as Ta, Mo, Ge and SiO₂. A highly crystalline h-BN obtained by Suzuki (1988) on a well-oriented-graphite-film-coated Ni substrate indicates that higher T_d might have been used in this case, while Grauleau (1981) used a mixture of B₂H₆ (or B₂H₅Br, B₂H₅Cl, B₂H₇N) with NH₃ and alcohol or ether in the ratio 1:20:9 at high temperature (T_d ≥ 1600°C) and low pressure to deposit isotropic BN on graphite or BN substrates.

A broad range of NH₃/B₂H₆ ratios (α) was used. Similar to the BCl₃ + NH₃ mixtures, the reactant gases (B₂H₆ and NH₃) were usually brought to the reaction chamber using separate tubes.

The deposition rate was found to increase with T_d, exhibiting Arrhenius behaviour at least to 700°C, above which it became independent on T_d. It increases with partial pressure of diborane (Murarka 1979, Adams 1980), but its dependence on partial pressure of NH₃ is not clear: according to Murarka (1979), it is proportional to D(NH₃)^{-1/5}, and according to Adams (1980) it is independent on it. Other deposition conditions (flow-rate, α) also influence deposition rate (Murarka 1979).

The chemical composition of the deposit, its crystal structure and other properties depend on conditions of its preparation. At low T_d (340°C) and using $\alpha > 0.5$ an amorphous product is formed, the composition of which can be expressed by the formula B_6NH_x (Adams 1980). Rand (1968) found residual B-H bonding at 600°C. For low α values (i.e. with excess B_2H_6) a deposit containing free B in addition to BN is formed, so that overall B/N ratio in the deposit may reach high values (up to 4, according to Murarka (1979)).

Crystallinity of the deposits obtained at low T_d is usually poor. Amorphous deposits are formed at T_d below 1000°C and polycrystalline at higher temperature.

Other properties of the coatings, prepared with a broad range of deposition parameters, are also very much different from each other, although they are generally well adherent to the substrate (except to Ge) and usually transparent or translucent.

One of the important factors influencing properties of the coatings is their B-content. The deposits richer in boron (obtained at lower T_d , low α values and higher flow-rates) have high values of refractive index (up to 2.8, Murarka 1979), or even 3.4 (Adams 1980). High α values (10 - 80, Rand 1968) lead to deposits apparently without free B and their refractive index values are 1.7 - 1.8 (similar to those obtained for BN coatings prepared from the $BCl_3 - NH_3$ mixtures, see 2.1, and to the values (1.78 - 1.9) obtained for B/N = 1 from β -trichloroborazine, Singh 1987). Other properties of thus obtained deposits are: electrical resistivity, $\geq 10^{14}$ ohm cm, dielectric strength about 5×10^6 V cm, dielectric constant (at 1 MHz) about 3.5.

All mentioned authors dealing with BN coatings prepared from the $B_2H_6 + NH_3$ (+ H_2 or N_2) gas mixtures found that the coatings could be used as electronic materials. Their possible applications such as B-diffusion sources, surface protection, Na-diffusion barriers, thin film dielectrics, passivation layers for use in various electronic devices have been mentioned. Other applications, e. g. masks for X-ray lithography, microwave windows (Adams 1981) have also been mentioned.

TABLE 2.2

BN coatings obtained from B_2H_6 and NH_3

Preparation conditions	Apparatus, substrate	Characteristics	Applications	Reference
1	2	3	4	5
H_2 or N_2 ; 600-1000°C, ambient P, $\alpha=10-80$	Vert., cold-wall; Si (mostly), Ta, Mo, Ge, SiO_2	Amorph., B-H band at $T_d=600^\circ C$, clear, vitreous, adherent (except Ge), smooth film, $\leq 0.6 \mu m$ thick; R incr. with $D(B_2H_6)$, decr. with $D(NH_3)$; band gap 3.8 eV, refractive index 1.7-1.8, diel. strength 5×10^6 V/cm, diel. constant at 1 MHz 3.5, $\rho \geq 10^{14} \Omega cm$	Semiconductor surface protection; Na diffusion barrier; B diffusion source; thin-film dielectric	Rand 1968
H_2 ; 700-1250°C, 5% B_2H_6 in H_2 ; $\alpha=1$	Si substrate	For low T_d amorph. BN, decomp. on heating in N_2 ; polycryst. at $T_d \geq 1000^\circ C$ (h-BN); $R=3 \mu m/h$ at $T_d=700^\circ C$; B diffuses into Si during deposition ($< 1000^\circ C$)	B diffusion source; planar diodes; MIS memory diode	Hirayama 1975
N_2 ($+PH_3$); 300-900°C, ambient P; $\alpha = 0.5-31$	Si substrate	Mixture BN + B, P-doped films; R incr. with T_d at 400-700°C, then independent; R incr. with $D(B_2H_6)$, with $D(NH_3)^{-1/5}$; R incr. with FR of reactant gases, incr. with $1/\alpha$; B/N from 0.7 to 4; refractive index 1.7-2.8 depends on B/N, $D(NH_3)$, FR; B-rich films are tensile, with high refractive index		Murarka 1979
N_2 ; 500°C	Si substrate	BN layer (20 nm) covered with Si_3N_4 (80 nm); heat treatment at 1200 creates B diffusion layer	B diffusion source; passivation layer	Shohno 1979
N_2 ; 250-600°C, 0.4-0.65 mbar	Horiz., hot-wall; Si substrate	Amorph.; B/N=6 for $T_d=340^\circ C$, $\alpha > 0.5$, i.e. B_6NH_x ; R incr. with $1/T_d$ at low T_d , then decr. (depletion), incr. with $D(B_2H_6)^{1/2}$, independent on $D(NH_3)$ and P; refractive index decr. from 3.4 to 2.3 for $\alpha=0$ to 0.5		Adams 1980

TABLE 2.2 continued

1	2	3	4	5
B_2H_6 , B_2H_5Br , B_2H_5Cl or $B_2H_7N + NH_3$ + alcohol or ether, $\geq 1600^\circ C$, ≤ 20 mbar	Graphite or BN substrate	Isotropic BN	Useful for constructing electron tubes	Grauleau 1981
$B_2H_6 + NH_3$	Fe-group metal or alloy coated by highly oriented graphite film (substrate)	Highly crystalline h-BN	Electronic material	Suzuki 1988

Designations: D(X) = flow-rate of X; FR = flow-rate; P = pressure; R = deposition rate; T_d = deposition temperature;
 ρ = electrical resistivity

Abbreviations: Amorph. = amorphous; cryst. = crystalline; decomp. = decomposes; decr. = decrease; diel. = dielectric;
 horiz. = horizontal; incr. = increase; polycryst. = polycrystalline; vert. = vertical

2.3 Preparation of BN coatings by thermal decomposition of single compounds containing both elements

Preparation of BN coatings by using two compound gases - one containing B but not N and the other containing N but not B - has some obvious disadvantages. Each compound has to be introduced separately in order to avoid premature chemical reactions, one or both components being introduced directly into the hot zone, close to the substrate. A consequence of such a procedure is an inadequate mixing of the gases, leading to a non-uniformity of the coating. This creates problems, in particular in the large scale production.

One possibility of avoiding such problems consists in using a single compound containing both B and N. To choose such a compound is not so simple, however, because of a number of requirements that should be satisfied. The compound should preferably have both elements in the 1 : 1 stoichiometric ratio, it should be volatile at temperatures close to room temperature, stable at or near room temperature, susceptible of thermal decomposition at elevated temperatures producing BN, and it should be commercially available and relatively inexpensive.

A group of compounds which generally satisfy these requirements, except the last one (to be inexpensive) are borazine, $B_3N_3H_6$ (B) and its derivatives hexachloroborazine, $B_3N_3Cl_6$ (HCB) and β -trichloroborazine, $B_3N_3H_3Cl_3$ (TCB). These cyclic compounds consist of planar, quasi-aromatic rings, similar to benzene and its derivatives. The last of these compounds, TCB, is the most suitable one. Chemical reactivity of these compounds, in particular their hydrolysis, and their high price are probably the reasons why a relatively small number of papers and patents deals with BN preparation from them. Certain authors have prepared the starting compound prior to its use, some of them (Gebhardt 1973) using it immediately, in stream with the CVD process.

Another advantage of this group of compounds with respect to the most usually applied $BCl_3 + NH_3$ mixture is in the fact that the latter involves rapid formation of solid intermediates which can be readily carried to an open, unobstructed deposition surface, but which do not diffuse to any depth prior to final pyrolysis and deposition, so that their use for infiltration of porous bodies is difficult if at all possible. In addition, since infiltration must proceed at relatively low deposition rates to prevent clogging of outer access parts of the porous body, long deposition times are required at constant conditions, which is impractical in the case of $BCl_3 + NH_3$ mixtures because of formation of NH_4Cl by-product clogging the furnace passages and exhaust lines. However, TCB and other similar compounds decompose to form BN and gaseous by-products, thus eliminating the problem of coping with a solid by-product. Also, at sufficiently low concentrations in

in the gas phase, premature settling out of solid intermediates can be avoided and penetration to inner deposition surfaces achieved.

In the procedures employed by different authors (Table 2.3) the compound used was introduced without any carrier gas, or with He or N_2 .

The range of temperatures used for the deposition is broad and extends from 300 to 1800°C. Low T_d leads to low deposition rates and to the products with chemical composition differing from that of BN (Adams 1981). Low pressure was mostly used for both CVD and CVI (infiltration).

The deposition rate increases with increasing T_d , being 2 - 2,5 times higher than with a $BCl_3 + NH_3$ mixture and reaching high values, up to 1.5 mm/h (Liepin 1975).

The deposits are usually transparent and their IR spectrum shows the usual absorption bands (at about 1400 and 800 cm^{-1}), except for the low-temperature deposited coatings, where B-H, NH_2 and NH absorptions are found (Adams 1981).

Gebhardt (1973) found that deposits formed between 1100 and 1500°C contained appreciable amounts of undecomposed borazine and/or incompletely pyrolysed fragments which were expelled by heating above T_d . According to the author, the amount of trapped volatile material is perhaps more dependent on the concentration of deposition species and deposition rate, than on T_d alone. Thus the deposit prepared at 1200°C and subsequently heat-treated shows far more complex spectra than the 1100°C deposit.

Refractive index of the deposits prepared at low T_d was found to vary between 1.75 and 2.15 (Adams 1981). The values in the range 1.78 - 1.9 found by Singh (1987) for the deposits with B/N = 1 are close to those found by other researchers for the same B/N ratio (Rand 1968, Takahashi 1981, Murarka 1979).

A variety of substrates (Si, SiO_2 , graphite, W, Mo, SiC, Al_2O_3 , BN etc.) used by different researchers shows that deposition of BN is not selective. However, the films on Si crack (Feurer 1980).

Crystallinity of the deposits was poor. Amorphous deposits were prepared at T_d up to 1100°C. Only at $T_d = 1800^\circ C$ crystalline deposits (h-BN) were obtained. The amorphous coatings become crystalline (h-BN) when treated at 1800°C, although their crystallinity remains smaller than in those deposited at 1800°C (Gebhardt 1973).

Infiltration of BN into porous substrates, such as BN-felt, 4D SiO_2 (Gebhardt 1973) and ceramic composites (SiC fibres in SiO_2 matrix, carbon

fibres in SiC, Al₂O₃ fibres in SiC) (Rice 1985) was effected at relatively low temperatures (900 - 1100°C). Infiltration of fibrous preforms (Gebhardt 1973) was found to be less complete than with carbon under comparable conditions, which is explained by higher deposition rate and probably lower diffusion rates in the case of TCB.

The advantage of infiltration of the mentioned ceramic composites by BN is illustrated by the 4 times greater strength and much higher toughness of the infiltrated SiC fibres/SiO₂ matrix composites (Rice 1985).

Somewhat different from the starting materials treated in this section is 1, 3, 5 - trimethoxyborazine (TMB) used in a mixture with NH₃ at T_d between 1500 and 1800°C at both low and atmospheric pressure to deposit isotropic BN (Branovich 1972). A deposition rate of 0.38 mm/h was obtained working at atmospheric pressure with NH₃/TMB ratio of 25.

TABLE 2.3

BN coatings obtained from borazine and its derivatives

Preparation conditions	Apparatus, substrate	Characteristics	Applications	Reference
1	2	3	4	5
$B_3N_3H_6$; 300-650°C, 0.1-1 mbar	Horiz., hot-wall, Si wafers	For $T_d < 550^\circ\text{C}$, NH groups present and deposit is reactive; for $T_d > 550^\circ\text{C}$ IR spectrum shows presence of BH groups; low R, incr. with T_d up to 550°C (depletion at higher T), incr. with P. Refr. index at $T_d = 500^\circ\text{C}$ incr. with P from 1.75 to 2.15	Unsuitable for X-ray lithography masks	Adams 1981
$B_3N_3H_6$; 900±50°C	CV Infiltration of SiC fibres/SiO ₂ matrix, carbon/SiC and Al ₂ O ₃ /SiC composites	BN coating on the fibres 0.05-several tenths of a micron thick; 0.1 µm coating on SiC fibres in SiO ₂ matrix leads to 4-fold incr. in strength and large incr. of fracture toughness	Better mechanical properties of composites	Rice 1985
$B_3N_3Cl_6$ prepared by the authors; 900°C, 10 ⁻⁴ mbar (subl. at 120°C in vacuum)	Horiz., hot-wall; SiO ₂ , Si	0.5-1 µm thick translucent films; R ≤ 250 nm/h; good adhesion on SiO ₂ , but cracks on Si; h-BN very poorly cryst.; No Cl	Corrosion-resistant, protective films	Feurer 1980
As in the foregoing article	Horiz., hot-wall; Si	Translucent to white films; composition close to BN, traces of Cl; IR normal of h-BN		Constant 1981
$B_3N_3H_3Cl_3 + N_2$; for CVD: 1100-1800°C, 4 mbar; for CV Infiltration: 1100°C, 4 mbar	BN-felt, 4-D SiO ₂	Colorless to light yellow, glassy, transparent; for $T_d = 1100^\circ\text{C}$ amorph., when HT to 1800°C becomes h-BN; for $T_d = 1800^\circ\text{C}$ more cryst. than above; adherent to BN felt		Gebhardt 1973

TABLE 2.3 continued

1	2	3	4	5
$B_3N_3H_3Cl_3$ or $B_3N_3H_3(C_4H_9)_3$ prepd. by the authors + He; 900-1650°C; 6.5-20 mbar	Graphite, W, Mo substrates	R incr. with T_d , incr. with D(He) and is 2 - 2.5 higher than from $BCl_3 + NH_3$; $R \leq 1.5$ mm/h		Liepin 1975
$B_3N_3H_3Cl_3$; 1050°C; closed tube conditions with TCB at one end and liq.- N_2 -T at the other; max P \approx 0.15 mbar	Horiz., hot-wall; SiO_2 , Si, SiC, Mo, Al_2O_3 , mullite, carbon	Non-selective deposition; amorph., transparent with IR spectrum of h-BN; when treated at 1700°C becomes h-BN; refractive index 1.78-1.9; B/N = 1		Singh 1987
1,3,5-trimethoxyborazine + N_2 + NH_3 ; 1500-1800°C, 13-65 mbar or ambient P; α =8-25	Graphite chamber	At 1650°C, ambient P and α =25, isotropic BN obtained; $R=0.38$ mm/h	Preparation of isotropic BN	Branovich 1972

Designations: D(X) = flow-rate of X; HT = heat treated; IR = infrared; R = deposition rate; T = temperature; T_d = deposition temperature

Abbreviations: amorph. = amorphous; cryst. = crystalline; horiz. = horizontal; incr. = increase; liq. = liquid; prepd. = prepared; refr. = refractive; subl. = sublimate

2.4 Plasma-assisted CVD of BN

Conventional CVD procedures have a disadvantage in requiring high substrate temperatures (above 1000°C), which makes them unsuitable for lower melting-point materials, such as heat-treated metals. In the plasma-assisted CVD (PACVD) the substrate can be kept at low temperature because chemically active species, such as ions and free radicals, acquiring energy in the electric field, react to produce the deposit. These species are produced either in the gas phase, through electron-molecule collisions, or at solid surfaces, through the impingement of ions and electrons produced in the plasma. Fig. 3.1 shows that particles in the PVD processes have higher energy than those in the conventional CVD.

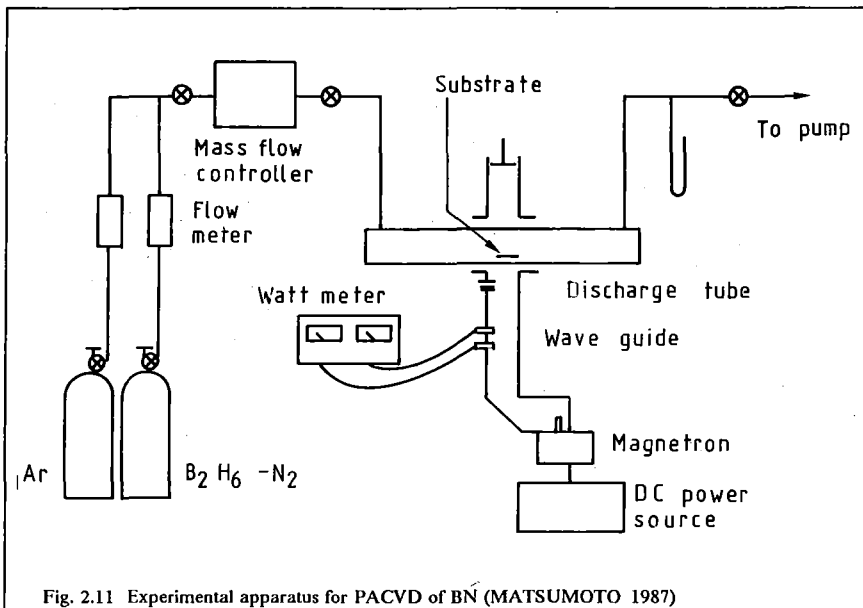
Recently the deposition of thin films by PACVD has graduated from the laboratory to production scale in the fields of microelectronics, optics and solar energy (Bell 1981). In many instances the film properties obtained by PACVD are unique and cannot be achieved by other deposition techniques. However, because of reduced pressures, deposition rates are relatively low. Also, due to the radiation environment of a glow discharge, defect creation in substrates and/or films often occurs.

In most instances PACVD is carried out in a low pressure plasma sustained by a high-frequency electric field. The electron temperature is typically $>10^4$ °C, while the gas temperature is between room temperature and 300°C.

Chemical reactions involved in PACVD of BN may be different from those in the conventional CVD, because species in excited radical and ionic forms may react with the molecules of NH_3 , boron-containing compound, N_2 and H_2 . Thus, by varying the conditions of the PACVD process (pressure (P), electrical source power and the NH_3 /B-containing-compound ratio (α)), the optimum conditions for the formation and deposition of BN can be achieved.

An experimental apparatus for PACVD of BN is presented schematically in Fig. 2.11. In a relatively few papers concerned with PACVD of BN, gas mixtures $\text{NH}_3 + \text{B}_2\text{H}_6 + \text{H}_2$ (a few per cent of B_2H_6 in H_2) (Yuzuriha 1985 and 1986, Hyder 1976), $\text{NH}_3 + \text{BCl}_3 + \text{Ar}$ (Gafri 1980), or $\text{NH}_3 + \text{BH}_3 \cdot \text{N}(\text{C}_2\text{H}_5)_3 + \text{Ar}$ (Schmolla 1982) were used. The P and α values were similar to those in the conventional LPCVD procedures (P between 0.1 and 6.5 mbar, α between 1 and 8, except in Miyamoto's (1983) experiments with $\alpha = 16$), while substrate temperature was up to 620°C, except in the work of Hyder (1976) who used temperatures up to 1000°C (Table 2.4). Different substrates were used: die steel, stainless steel, Si, GaAs, well-oriented pyrolytic graphite and PBN.

The plasma power between 4 and 150 W was used, frequency being 13.56 MHz, except in Gafri's experiments (1980) in which 0.5 MHz was used. Schmolla



(1982) has employed a two-plasma-zone system, one zone with high power (150 W, 13.56 MHz) in which the (high temperature) chemical reactions take place, and the other (15 W, 27.12 MHz) where deposition on the (cool) substrate proceeds.

The deposition rate (R) is generally low (0.1 to 0.5 $\mu\text{m/h}$). It increases with T_d , decreases with α , is independent on substrate nature (Hyder 1976) and depends on magnetic field (Yuzurika 1986). It increases with P up to 0.65 mbar (Yuzurika 1985), but decreases with P in the 1.3 - 6.5 mbar range (Gafri 1980).

The deposits are typically transparent, amorphous (except at higher T_d), smooth and without pinholes. Their structure depends strongly on T_d : below 600°C the films are essentially amorphous but short-range order with hexagonal bonds is predominant (Miyamoto 1983), while above 600°C polycrystalline material is formed. Hyder (1976) reports that the films obtained are more crystallized (with h-BN single crystals on the well-ordered substrates) than those obtained by the conventional CVD at higher T_d , and Yuzurika (1986) has found that magnetic field promotes deposition of h-BN.

Stoichiometry of the PACVD BN films depends mostly on the α ratio. According to Hyder (1976), stoichiometric BN has been prepared at 1000°C with $\alpha = 7$, below this α value the deposit is B-rich and for $\alpha = 8$ a N-rich deposit is obtained, while Yuzurika (1986) obtained the B/N ratio closer to 1 ($B/N = 1.7$) for $\alpha = 4$, than for $\alpha = 1$ ($B/N = 3.4$), and Miyamoto (1983) reported stoichiometric films for $\alpha > 7$.

The IR spectra of the films deposited below 300°C contain absorption bands due to B-H and N-H vibrations, indicating that such deposits are chemically different from BN. A comparison of the conventional CVD with PACVD shows that in the former the N-H bonding is detected up to $T_d = 600^\circ\text{C}$, while in the latter no N-H absorption is observed above about 300°C, possibly because of hydrogen desorption provoked by the ion bombardment (Yuzurika 1986). In this respect a result of Gafri (1980) should be mentioned: the films deposited at 550°C contain Cl, but no Cl is detected in the deposits prepared at 620°C.

A few data reported on electrical and optical properties of the PACVD films are more or less similar to those for the conventional CVD films. Thus, resistivity of the films of 2×10^9 ohm cm has been found, relative dielectric constant 2.7 to 7.7, breakdown 7×10^6 V/cm, optical band gap 5.0 - 5.8 eV, refractive index about 1.7 for near-stoichiometric films and up to 2.8 eV for the non-stoichiometric ones (Table 2.4).

Deposition of BN in a microwave discharge (MWCVD) (Matsumoto 1987) can be

regarded as a variant of PACVD. Reaction of B_2H_6 with nitrogen was used to deposit BN on quartz and Si substrates. An essential difference in the film properties with respect to those obtained by both conventional and plasma-assisted CVD is that by the MWCVD the cubic and hexagonal wurtzite BN films could be obtained, which makes this method closer to the reactive PVD ones.

The transparent BN, believed to be h-BN (graphite type) was found in thinner deposits obtained after short time (1 h), but experimental evidence (IR, XPS X-ray diffraction) shows that the deposits obtained after long time (20 h) consist of cubic and hexagonal wurtzite type BN. The proposed mechanism of formation of these phases is that NH and BH radicals (detected in the plasma by emission spectroscopy) are first adsorbed on the substrates and then react producing BN.

TABLE 2.4

BN coatings prepared by Plasma-assisted CVD

Preparation conditions	Apparatus, substrate	Characteristics	Applications	Reference
1	2	3	4	5
$B_2H_6 + N_2 + NH_3$; r.f. plasma, 13.5 MHz, 4 W coupled with capacitive coupler; substrate heated independ. $>700^\circ C$; 0.4-1.3 mbar	Si, compression-annealed PG and pyrolytic BN as substrates	Smooth, transparent, better cryst. than obtained by CVD at higher T_d from $B_2H_6 + NH_3$; R incr. with T_d , decr. with α , independent on subs.; $R=18-48 \mu m/h$, highest upstream; B-rich, except for $\alpha=8$ (N-rich), stoichiometric at $1000^\circ C$, $\alpha=7$; $\rho \approx 2 \times 10^9$ ohm cm, diel. constant 2.7-7.7; single h-BN cryst. obtained (largest on PG) best with $770-1000^\circ C$, $\alpha=8$		Hyder 1976
$BCl_3 + NH_3 + Ar$; r.f. plasma, 0.5 MHz; $550-620^\circ C$, 1.3-6.5 mbar, $\alpha=8$	Horiz. Pyrex reactor, die steel, graphite	Amorph. with small amount of h-BN; R decr. with incr. P ($R_{max} \approx 14 \mu m/h$); ICl present at $550^\circ C$ and higher P, but not at $620^\circ C$	Thermal insulator; die wash material; lubricant; P transmission medium	Gafri 1980
$BH_3 \cdot N(C_2H_5)_3 + NH_3 + Ar$; Two-plasma-zone system: I-13.56 MHz, 150 W, gas T $650^\circ C$; II-27.12 MHz, 15 W, subs. T $300^\circ C$; P=1-1.5 mbar	Ar carries org. compd. into I, then into II zone. Subs. in II zone; GaAs	Chem. stable BN films, excellent uniformity; No carbon; diel. constant 3.5, breakdown 7×10^6 V/cm	Insulator for T-sensitive semiconductors (GaAs) or device structures; masking	Schmolla 1982
$B_2H_6 + NH_3 + H_2$; 3-40 W r.f. plasma; subs. T $300^\circ C$, 5 mbar, $\alpha=1-16$	Vert.; Si, quartz	Amorph. for $\alpha=2-16$, h-BN-like short-range order; for $\alpha > 2.7$, B/N ≈ 1 with diel. constant 6.5, breakdown $> 3 \times 10^6$ V/cm; opt. band gap ≈ 5.0 eV; NH groups present		Miyamoto 1983
$B_2H_6 + NH_3 + H_2 + Ar$; 10-70 W, 13.56 MHz r.f. plasma, 84 G magn. field parallel to elec.; subs. T $400^\circ C$, 0.13-0.9 mbar, $\alpha=1-3$	Stainless steel plates, 5.7 cm diam., separated 2.9 cm	R incr. with P up to 0.65 mbar ($R_{max} = 0.18 \mu m/h$)		Yuzuriha 1985

TABLE 2.4 continued

1	2	3	4	5
B ₂ H ₆ + H ₂ ; 30 W, 13.56 MHz r.f. plasma? subs. T 400°C, 0.5 mbar, α = 1-4; magn. field normal to elec.	Stainless steel plates, 5.6 cm diam., separated 2.9 cm	Amorph., smooth films, no pinholes, contain O (<4%) and C (<2%); B/N=1.7 and 3.4 for α=4 and 1, respec.; R=0.13 μm/h, decr. with decr. P, affected by magn. field; for T<300°C, NH present; magn. field and α=4 promote h-BN; opt. band gap 5.6-5.8 eV, ref- ractive index ≈ 1.7 for α ≥ 4, incr. up to 2.8 for lower α; opt. properties not influenced by magn. field.		Yuzuriha 1986
<u>Microwave CVD</u> B ₂ H ₆ + N ₂ / Ar; 100 W, 2450 MHz; 200°C, 1.3 mbar	Si, quartz as subs.	After 1 h: transparent h-BN; after 20 h: cubic and hexagonal wurtzitic BN		Matsumoto 1987

Designations: P = pressure; PG = pyrolytic graphite; R = deposition rate; T = temperature; T_d = deposition temperature

Abbreviations: amorph. = amorphous; chem. = chemical; compd. = compound; cryst. = crystal, crystalline; decr. = decrease;
diam. = diameter; diel. = dielectric; elec. = electric(al); horiz. = horizontal; incr. = increase;
independ. = independent; magn. = magnetic; opt. = optical; org. = organic; respec. = respectively;
subs. = substrate; vert. = vertical

2.5 Preparation of BN coatings by other CVD techniques

This section contains data on i) starting materials used in conventional CVD other than those described in sections 2.1 - 2.3; ii) other techniques of CVD.

Other starting materials used in conventional CVD

Besides borontrichloride and diborane used in combination with ammonia to produce BN by conventional CVD methods, boronfluoride has been used.

The already mentioned thermodynamic and experimental study made by Hannache (1983) has led to the conclusion that in the $\text{BF}_3 + \text{NH}_3$ system the deposit contains only pure BN, but that no deposit is formed at high temperatures. However, even at low temperature (1100°C) a substantial percentage of BF_3 remains unreacted at the equilibrium regardless of the initial composition (in contrast to the $\text{BCl}_3 + \text{NH}_3$ system in which a much smaller amount of unreacted BCl_3 is only found for $\alpha < 1$). Nevertheless, the $\text{BF}_3 + \text{NH}_3$ system was found to be the most appropriate one for CVI, but the temperature range was limited to 1100-1200°C, because at higher temperatures a severe attack of carbon and graphite takes place (with formation of HCN).

Pierson (1975) used $\text{BF}_3 + \text{NH}_3$ mixture to prepare the composites BN fibres/BN matrix at 1100-1200°C and 40-50 mbar. The h-BN was found to be formed.

The same gas mixture was used (in addition to the $\text{BCl}_3 + \text{NH}_3$ one) by Kawai (1986).

Other CVD techniques

A new variant of the CVD technique, Molecular flow CVD (MFCVD), has been proposed by Nakamura (1985). The method applies pressures below 10^{-3} mbar and has the advantage that composition of the BN films obtained can be easily controlled by changing the ratio of the separately introduced reactant gases (NH_3 and decaborane, $\text{B}_{10}\text{H}_{14}$). The author used Si, sapphire and Ta as substrates and their temperature could be regulated by separate heaters in the range 300-1200°C.

The colourless and transparent films obtained are amorphous. The films prepared at 300°C show only the absorption bands due to NH, BH and NH_3 , but IR spectra of the films deposited above 700°C show the characteristic absorption bands of BN. From the optical absorption measurements it is estimated that the energy gap is 5.90 eV, in agreement with the values reported by other authors (see 2.1.2). For the B/N atomic ratio greater than 1.33 the non-stoichiometric films, being a mixture of B and BN phases are produced.

The composition of the films prepared at high temperature is proportional to the ratio of partial pressures $\text{NH}_3 / \text{B}_{10}\text{H}_{14}$.

Another method, named Electron-enhanced CVD, makes use of the electrons generated by field emission to assist in the conventional CVD method (Sokolowska 1986). The $\text{B}_2\text{H}_6 + \text{H}_2 + \text{N}_2$ gas mixture under 1 - 3 mbar pressure was introduced into a chamber similar to that of a conventional CVD apparatus. Near the substrate made of Si or Mo and kept at 600-1200°C was a tungsten tip generating electrons, the Bennet electric field (E_B) amounting to 6.4×10^5 V/cm. The cubic BN was obtained at $T_d \geq 900^\circ\text{C}$ and $E_B \geq 1.98 \times 10^5$ V/cm, whereas in the absense of the electric field only the h-BN was observed.

3. BORON NITRIDE PREPARED BY PHYSICAL VAPOUR DEPOSITION

In physical vapour deposition (PVD) coatings are produced on solid surfaces by condensation of elements or compounds from the vapour phase, whereby the deposit has identical composition as the vapour. However, for making coatings of high melting point compounds, the reactive PVD techniques must be used. In these processes metal vapours are produced in the presence of a partial pressure of the reactive gas to form a solid compound either in gas phase or on the substrate as a result of a reaction between the metal vapour and the gas atoms.

The PVD process takes place in vacuum chamber in which the residual pressure is 10^{-5} to 10^{-7} mbar. For the reactive PVD, partial pressure of the reactive gas is usually 10^{-2} to 10^{-3} mbar.

In the PVD process vapours are produced in two main ways:

- evaporation
- sputtering

In the evaporation process material to be evaporated is located in a source which is heated either thermally or using an electron beam.

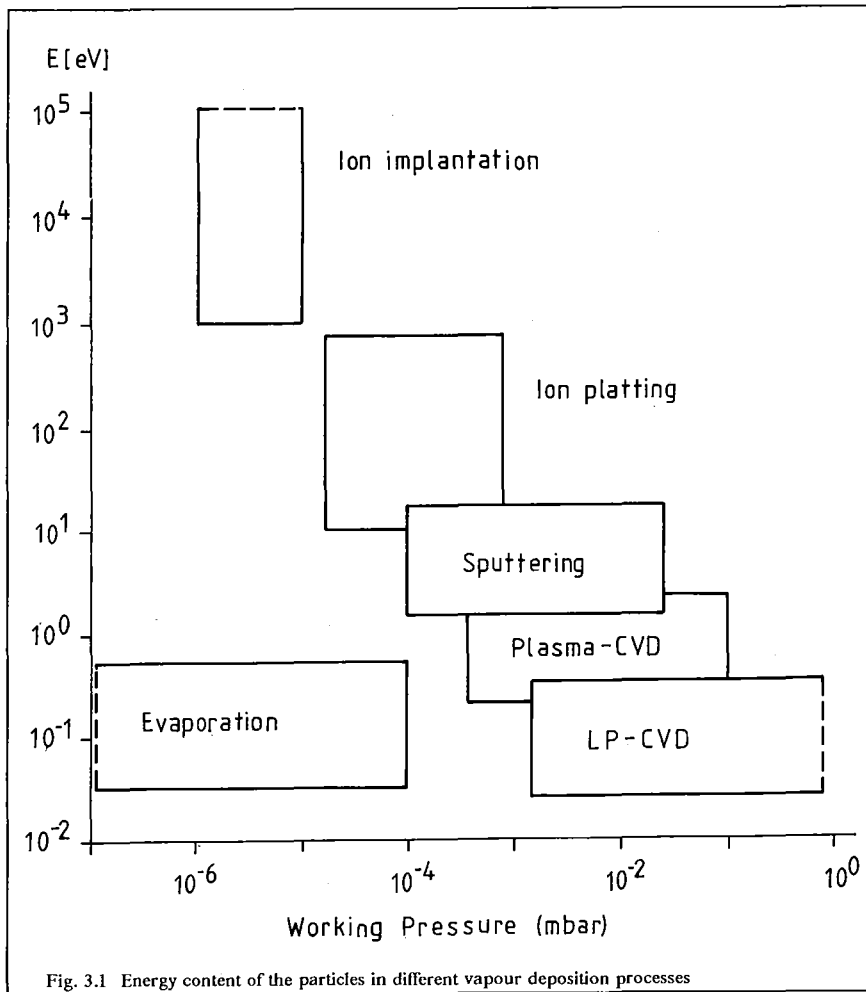
In the sputtering process vapours are produced by bombarding the solid surface (target) with high energy particles, usually Ar ions. The sputtering process takes place in a vacuum chamber in which are placed both the target, being the negative electrode (cathode), and substrate carrier, serving the purpose of an anode. For sputtering either dc voltage or high-frequency (usually radio frequency - r.f.) are used.

In the PVD process the substrate is at room temperature or heated at 200 to 500°C.

In the sputtering process the substrate can be on ground potential or on some negative (bias) potential.

During evaporation the substrate to be coated can be exposed to ion bombardment before and during deposition. Due to acceleration in the electric field, the particles are loaded with a high amount of kinetic energy and penetrate more or less deeply into the substrate (ion plating). Energy content of the particles in different vapour deposition processes is shown in Fig. 3.1.

In order to prepare BN coatings by PVD process, different starting materials and methods can be used:



- Reactive sputtering of BN in N_2
- Reactive evaporation of B in NH_3
- Reactive evaporation of H_3BO_3 in NH_3
- Reactive evaporation of $B_3N_3H_6$

3.1 Reactive sputtering of BN target in N_2

In order to prepare BN coatings BN can be used as a starting material. Due to high melting point of BN simple evaporation process can not be used. Instead, r.f. sputtering is usually employed.

In order to prepare stoichiometric BN coatings, the reactive r.f. sputtering from BN target has usually been performed in nitrogen gas; otherwise B-rich coatings would be obtained.

The deposition conditions and properties of BN coatings reported by different authors, are presented in Table 3.1. It can be noted that no data concerning application are given by the authors.

From Table 3.1 it can be seen that r.f. sputtering process is performed in conventional r.f. sputtering units, with pressure ranging from 10^{-6} to 10^{-7} mbar, before Ar and reactive N_2 gas are introduced and their partial pressure in the range of 10^{-2} to 10^{-3} mbar established. The r.f. power of the BN target is 300 to 600 W, the resulting deposition rate being about 5 nm/min, which is rather low and therefore a long time is needed to prepare coatings with a necessary thickness. Presumably, this is the reason that thicknesses of the BN coatings, presented in the Table 3.1 are less than or equal to 1 μm .

The substrate for BN coatings (glass, Si, sapphire, carbon, Ta) is at room temperature or heated up to 350°C.

If the substrate is at room temperature and at ground potential, the BN coatings are amorphous (Puychevriier 1976, Yasuda 1985, Seidel 1987). With substrate bias potential, even at room temperature crystalline h-BN (Rother 1985) or c-BN (Goranchev 1987, Seidel 1987) coating is obtained.

Sputtering from BN target can be performed by using Q-switched neodymium glass laser in N_2 gas. In this manner h-BN + c-BN coatings can be obtained, but no data are given about substrate temperature (Kessler 1987).

TABLE 3.1

BN coatings obtained from BN target and reactive gas

Method 1	Reactive gas 2	Working conditions 3	Properties of BN coatings 4	References 5
Reactive sputtering	Ar + N ₂	BN target 5x5 cm. Residual pressure in the chamber 10 ⁻⁷ mbar; P _{Ar} = 10 ⁻⁴ mbar; P _{N₂} = 6x10 ⁻³ mbar. Si substrate at room temperature or heated.	h-BN 300 to 600 nm thick. Optical absorption of as-prepared films is at 250nm. In annealed films optical absorption shifts to shorter wavelengths (220 nm).	Noreika 1969
Reactive r.f. sputtering	N ₂	The films are obtained in MRC sputtering unit.	Amorphous BN films.	Puychevriier 1976
Reactive r.f. sputtering	Ar + N ₂	The chamber was evacuated to 6.5x10 ⁻⁷ mbar; Ar/N ₂ mixture with total pressure 10 ⁻⁴ mbar. BN target 12.7 cm Ø, r.f. power 300 W. Anode/cathode spacing 9 cm; dep. rate 5 nm/min. Substrates (Glass, Si, Sapphire) at room temperature.	Thickness about 1 µm; B/N ratio 1.1 to 1.4. Colourless films. IR absorption at 1400 cm ⁻¹ . Band gap 5.4 to 5.6 eV.	Wiggins 1984
R.F. sputtering	Ar (93%) + H ₂ (7%)	Residual pressure 3.5x10 ⁻⁷ mbar. Target-to-substrate distance 2 cm; r.f. power 50 to 200 W. Substrates (Si, Quartz, Be) at room temperature.	Amorphous films 0.08 to 2.7 µm thick; good thermal stability up to 850°C. B/N ratio 1.13. IR absorption at 1400 cm ⁻¹ .	Yasuda 1985
Reactive r.f. sputtering	N ₂ or Ar + N ₂	h-BN target; r.f. voltage 800 to 1400 V. Fused quartz substrate at biased potent. - 100V.	h-BN films 60 to 80 nm thick. B/N ratio 1.1; BN films are stable in HF, H ₃ PO ₄ , NaOH and Ca(OH) ₂ at room temp. for 4 h. Destroyed by H ₃ PO ₄ + HNO ₃ at 140°C.	Rother 1985

TABLE 3.1 continued

1	2	3	4	5
R.F. sputtering	Ar or Kr	Substrate (Glass, Si, Al_2O_3) on biased potential.	c-BN films, 500 nm thick. B/N ratio 1.1 to 1.2; high stress.	Goranchev 1987
Reactive r.f. sputtering	Ar + N_2	Ar + N_2 total pressure 2×10^{-2} mbar. BN target, 650 W. Deposition rate 5 nm/min; Substrates (Carbon, Ta, Si) at biased potential -100 to -300 V, at room temperature.	Non stoichiometric films in pure Ar; with $P_{\text{N}_2} = 1 \times 10^{-2}$ mbar B/N = -1. With no substrate bias amorphous films; with - 300 V, c-BN. IR absorption peaks at 800 and 1400 cm^{-1} .	Seidel 1987
Q-switched neodymium glass laser (1J; 20 ns; repetition rate 1/min)	N_2	BN target. Power density 1 GW cm^{-1} . Target/substrate distance 12 cm. Pressure = 10^{-5} mbar, refilled with N_2 0.26 mbar.	Coatings consisting mainly of wurtzite BN with small admixture of h-BN; IR absorption peaks at 800, 1100 and 1400 cm^{-1} .	Kessler 1987

3.2 Reactive evaporation of boron in NH_3

For preparation of BN coatings boron (B) and ammonia (NH_3) can be used as starting materials.

The deposition conditions and properties of BN coatings prepared by this procedure, as reported by different authors, are presented in Table 3.2. Again, no data regarding application of BN coatings are mentioned.

The evaporation of a boron powder by electron beam in NH_3 environment gives reasonably high deposition rate and high thicknesses (5 - 10 μm). However, thick BN coatings exhibit compressive stress (Rother 1986) and are peeled off.

Another way to prepare BN coatings is to use B-target and $\text{N}_2 + \text{H}_2$ mixture. The gas mixture is pulsed into the vacuum chamber and a powerful electric discharge (100 J for 0,6 ms) is established between the boron and Cu electrodes. Wurtzite and "shock wave compressed" BN coatings have been obtained (Sokolowski 1979).

The best way to produce well-defined c-BN coatings is reactive ion plating (Weissmantel 1980 and 1982, Satou 1983). Boron was evaporated by electron bombardment in a residual atmosphere of N_2 . The ionized species are accelerated with bias voltage (Fig. 3.2). Grow rate 90 to 120 nm/min. By this procedure BN coatings 1 to 2 μm thick are produced in reasonable time. These BN coatings exhibit microhardness 30 GPa (Weissmantel 1980 and 1982) and electrical resistivity 10^{14} ohm cm (Satou 1983).

If deposition is performed with sufficiently high energy, c-BN coatings can be obtained even at room temperature (Satou 1983).

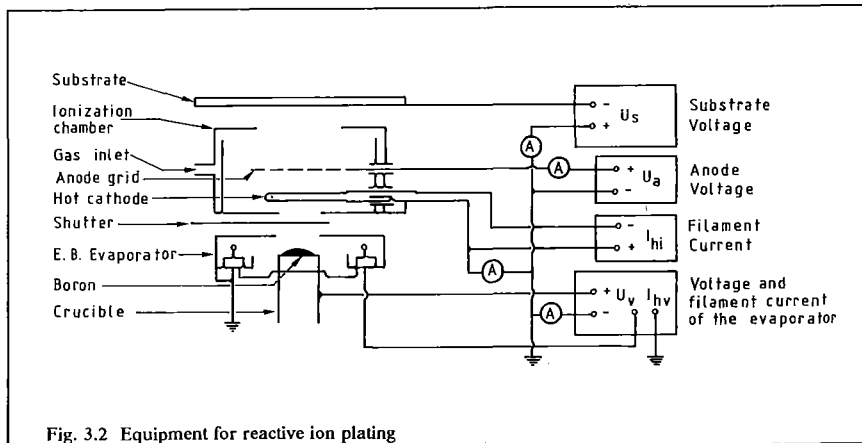


TABLE 3.2

BN coatings obtained from boron and reactive gas

Method	Reactive gas	Working conditions	Properties of BN coatings	References
1	2	3	4	5
Reactive pulse plasma crystallization	$N_2 + H_2$ 3:1	Boron target. N_2+H_2 gas mixture was pulse injected into chamber, pressure 10^{-7} mbar. Strong electric discharge (100 J, 0.6 ms) is then operated.	Wurtzite and "shock wave compressed" BN coatings.	Sokolowski 1979
Reactive ion plating	N_2	Boron is evaporated in a residual atmosphere of N_2 , pressure 10^{-3} mbar. The ionized species are accelerated with bias voltage of 500 to 3000 V. Grow rate 90 to 120 nm/min. Substrate at $200^\circ C$.	Thickness 1 to 2 μm . If films are deposited with high ion energies, c-BN coatings are obtained. Microhardness 30 GPa.	Weissmantel 1980
Reactive ion plating	N_2	Electron beam evaporation of boron in nitrogen. Substrate - hard alloys.	c-BN Microhardness 30 GPa.	Weissmantel 1982
Reactive ion plating	N_2	Boron was evaporated by electron bombardment. The N_2 ions were accelerated onto substrate in vacuum of 4×10^{-5} mbar. Substrate at room temp.	With B/N ratio less than 1.8 BN films are amorphous. With B/N ratio 2.5 films consist of c-BN. Electrical resistivity 10^{14} ohm cm.	Satou 1983
Electron beam evaporation	NH_3	Boron powder was electron-beam-evaporated in NH_3 environment. (Residual pressure 10^{-6} mbar; NH_3 pressure 10^{-4} mbar). Substrate (Al, Si, NaCl, quartz) at room temp. or at $400^\circ C$.	Thickness 5 to 10 μm . Microhardness 30 GPa. High compressive stress.	Rother 1986

3.3 Reactive evaporation of H_3BO_3 in NH_3

The BN coatings can be produced by evaporation of boric acid (H_3BO_3) in NH_3 plasma. The evaporation has been performed from a thermally heated Mo-boat and NH_3 gas is introduced into the vacuum chamber (Fig. 3.3). The plasma is generated by accelerating the thermoionically emitted electrons from a heated W-filament (Lin 1987).

In another procedure an external magnetic field enhances the plasma and also sustains the discharge in vacuum of cca 10^{-4} mbar (Chopra 1985). Boron from the decomposed boric acid reacts with N_2 in the gas phase and produces the BN coatings at unheated or heated from 200 to 500°C substrate (Table 3.3). At a substrate temperature below 200°C the BN coatings are amorphous. At higher substrate temperature c-BN films are obtained. The adherence of the BN coatings deposited at substrate temperatures above 400°C is good. The microhardness of the BN coatings is 21 GPa (Chopra 1985) or 34-36 GPa (Lin 1987).

3.4 Ion beam deposition from borazine

Borazine ($B_3N_3H_6$) vapour was used as a starting material to prepare BN films. Plasma discharge is maintained by electrons from the hot W-cathode that are attracted to the anode. Before reaching the anode, these electrons collide with and ionise neutral borazine. The total pressure during deposition was cca 10^{-4} mbar. Deposition rate 6-12 nm/min. The substrates (WC, Al_2O_3 , glass, steel) at room temperature. Hard and adherent c-BN films were produced at room temperature. Microhardness 22-31 GPa (Shanfield 1983).

It has been found that by this process can be obtained c-BN films with relatively strong interfacial adhesion and high friction (Miyochi 1985).

Using the same process, but with charge neutralization, smooth, uniform and adherent BN coatings were obtained (Halverson 1985) (Table 3.4, Fig. 3.4).

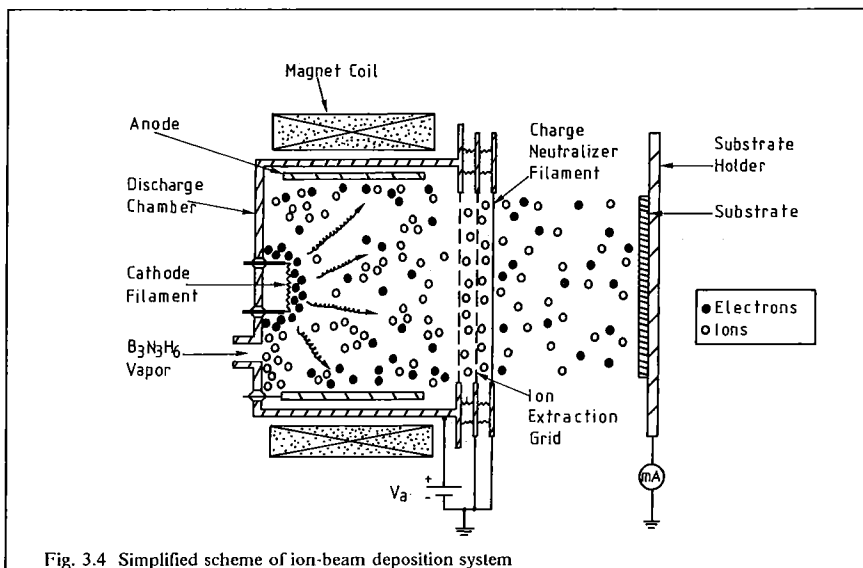
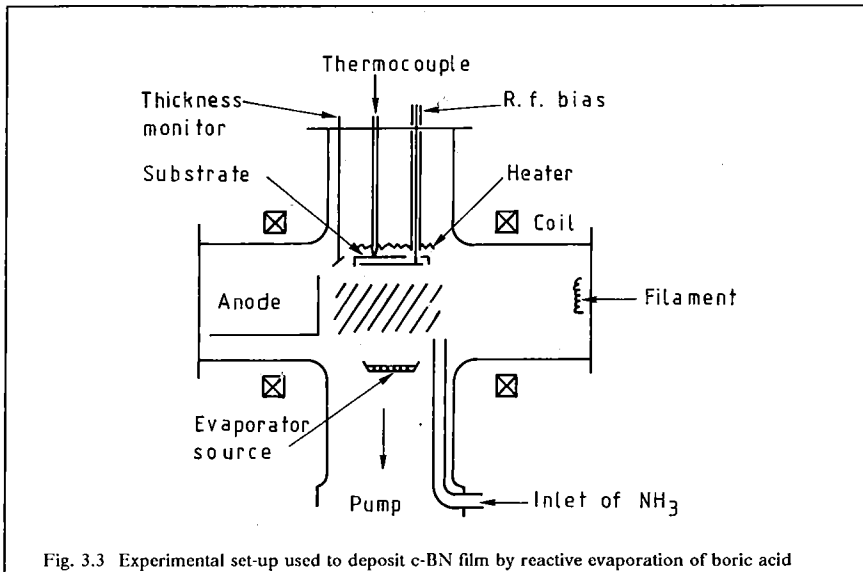


Table 3.3
BN coatings obtained from boric acid and NH_3

Method	Working conditions	Properties of BN coatings	References
Activated reactive evaporation	H_3BO_3 is evaporated by a resistance-heated filament. The vapour passes through the plasma and is decomposed to react with NH_3 , introduced into the chamber. An external magnetic field enhances the plasma and also sustains the discharge in vacuum of 6×10^{-4} mbar. Dep. rate 150 nm/min. Substrate at 200-500°C.	At temperature below 200°C, BN is amorphous; at higher temperature c-BN is obtained Adherence of the films is good at deposition temp. above 400°C. Microhardness 21 GPa.	Chopra 1985
Activated reactive evaporation	Evaporation of H_3BO_3 from Mo-boat, in NH_3 plasma. The plasma is generated by accelerating the thermionically emitted electrons from a heated W-filament. Substrate at biased potential and 450°C.	c-BN, colourless, 500 nm thick. Refractive index 2.0-2.3. High transmission in UV and VIS. IR absorption at 1400 cm^{-1} . Microhardness 34-36 GPa.	Lin 1987

Table 3.4

Ion beam deposition from borazine

Method	Working conditions	Properties of BN coatings	References
Ion beam deposition	Borazine gas is injected into vacuum chamber, with ultimate pressure of cca 10^{-7} mbar. During BN deposition the pressure is cca 10^{-4} mbar. The ion beam energy 150 - 1800 eV. Deposition rate 6-12 nm/min. Substrate at less than 300°C.	c-BN, 1 μ m thick. Microhardness 21-28 GPa.	Shanfield 1982
Ion beam deposition	Same as foregoing	c-BN films, 2 μ m thick, with relatively strong adhesion and high friction	Miyochi 1985
Ion beam deposition	The same procedure as in foregoing two articles, but deposition performed with charge neutralization. Deposition rate 3-10 nm/min.	c-BN with B/N = 1. Smooth, uniform and adherent film, 1,8 μ m thick.	Halverson 1985

3.5 Influence of deposition conditions on BN coating properties

A broad range of deposition conditions used by different authors had as a consequence a variety of properties of BN coatings.

Stoichiometry

The composition of BN films deposited by ion beam process from borazine corresponds to the stoichiometric BN (Shanfield 1985), containing different amounts of oxygen and carbon (Halverson 1985). The B/N ratio in BN coatings prepared by reactive sputtering process is always greater than unity (1.1 - 1.3) (Wiggins 1984, Rother 1985, Yasuda 1985), while in the BN coatings prepared by ion plating process from boron it is about 2.5 (Satou 1983).

Crystal structure

If substrate is at room temperature during sputtering process, BN coatings are amorphous (Puychevri r 1986, Yasuda 1985). If substrate is at room temperature but on some bias potential, BN coatings consist of h-BN (Rother 1985) or c-BN (Goranchev 1987, Seidel 1987) (Fig. 3.5). Cubic BN can be obtained if deposition is performed by reactive ion plating of boron (Weissmantel 1980 and 1982, Satou 1983), or by plasma activated reactive evaporation of boric acid (Chopra 1985, Lin 1987). The BN coatings prepared by ion deposition process from borazine are cubic as well (Shanfield 1982, Halverson 1985).

The energy content of the particles during the deposition process is certainly one of the main factors determining the crystal structure of the deposit. Apparently with higher energy wurtzite BN coatings can also be obtained (Sokolowski 1979). The sequence arranged so to correspond to increasing energy would be: amorphous BN, h-BN, c-BN. Whether wurtzite BN would be obtained with higher or lower energy than c-BN is not clear from the so far published results. Fig. 3.1 presents energy content of the particles in different PVD processes. The microstructure of the c-BN coating was found to be very fine grained one (Lin 1987).

Thickness

Thickness of the BN coatings obtained by reactive r.f. sputtering is usually below or about 1 μm (Noreika 1969, Wiggins 1984, Rother 1985, Weissmantel 1980). If target-to-substrate distance is small, the thickness may be higher, up to 2.7 μm (Yasuda 1985). With ion enhancement process, deposition rate is higher and thickness of the coatings amounts up to 5-10 μm (Rother 1986).

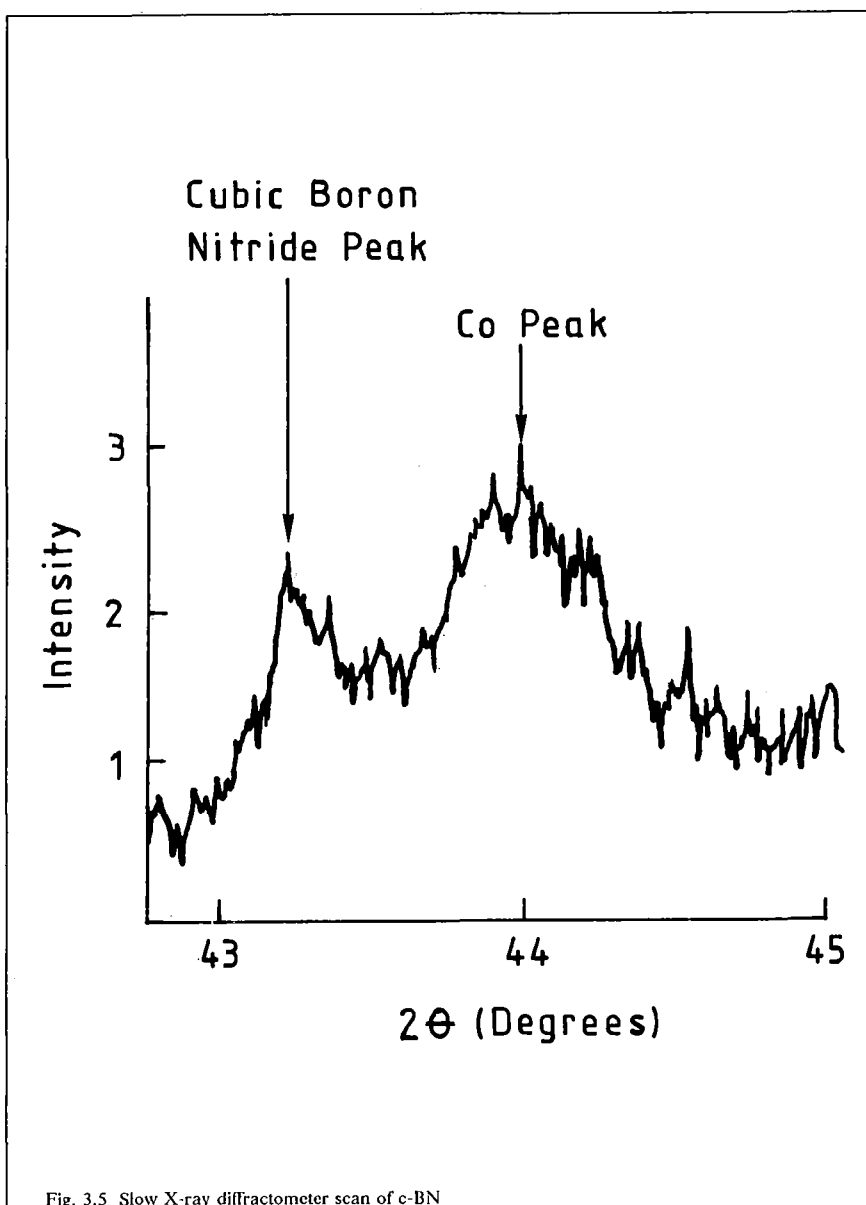


Fig. 3.5 Slow X-ray diffractometer scan of c-BN

Adherence

The adherence of the BN coatings is good if substrate is above 400°C (Chopra 1985). Thicker BN coatings exhibit compressive stress (Rother 1986) and peel off. The c-BN coatings 2 μm thick have relatively strong interfacial adherence and high friction (Miyochi 1985).

Microhardness

The microhardness of the BN coatings 1 - 2 μm thick is 30 GPa (Weissmantel 1980 and 1982). The same microhardness value have thicker coatings but they have high compressive stress (Rother 1986).

Optical properties

Colour of the BN coatings depends on the sputtering conditions. With increasing N_2 gas pressure during sputtering, colour changes from deep brown (pure Ar) via yellow (10 % N_2), to colourless (25-100 % N_2) (Wiggins 1984). The c-BN coatings are colourless according to Lin (1987).

Transmittance of c-BN films in UV is high and in the visible it is very high, $\geq 95\%$ (Fig. 3.6) (Lin 1987). Transmittance of c-BN coatings in the IR is also very high ($\geq 95\%$) (Fig. 3.7) (Chopra 1985).

The c-BN coatings show absorption peaks at 1400 cm^{-1} corresponding to B-N bonding vibrations and at 800 cm^{-1} corresponding to B-N-B stretching vibrations. With substrate bias the peak position is shifted from 800 cm^{-1} to 785 cm^{-1} and the peak at 1400 cm^{-1} shows no change (Fig. 3.8) (Seidel 1987).

The refractive index of the c-BN coatings is in the range 2.0 to 2.3 (Lin 1987).

Thermal properties

Amorphous BN coatings prepared at room temperature by r.f. sputtering from a sintered BN target have a good thermal stability up to 850°C. These films are desirable (Yasuda 1985).

Chemical properties

The h-BN films with thickness of about 60 to 80 nm, deposited by r.f. sputtering from a h-BN target in N_2/Ar atmosphere show chemical stability. The h-BN films obtained, when treated with aggressive fluids such as HF , H_3PO_4 , HNO_3 , NaOH or CaOH for 4 h at room temperature showed no difference in

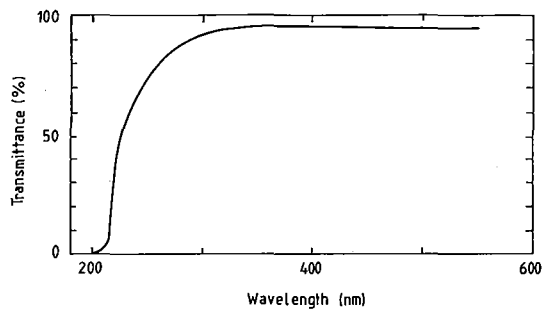


Fig. 3.6 UV-visible transmission spectrum of c-BN film 500nm thick, deposited onto quartz substrate at 450°C (LIN 1987)

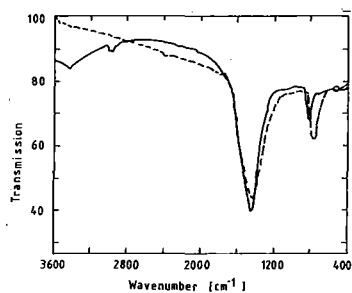


Fig. 3.7 Visible-IR transmission and reflection spectrum of c-BN film 400nm thick, deposited onto a glass substrate at 400°C (CHOPRA 1985)

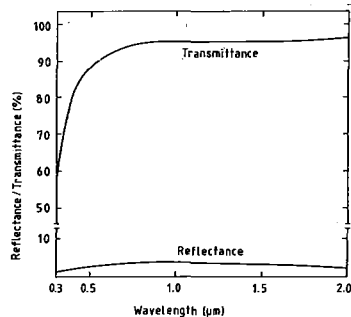


Fig. 3.8 IR absorption spectra of BN film —, no substrate bias; - - -, with substrate bias (SEIDEL 1987)

structure. Only in a mixture of H_3PO_4 and HNO_3 at a temperature of 140°C , the films were destroyed within a short time (Rother 1985).

Electrical properties

The electrical resistivity of the c-BN films 500 nm thick is about 10^{14} ohm cm (Satou 1983).

4. APPLICATIONS OF VAPOUR DEPOSITED BN

Although a number of papers and patents are dealing with numerous applications of BN prepared by CVD, i.e. with h-BN (Tables 2.1 - 2.4), there is hardly any mentioned application of the cubic (or wurtzitic) BN form.

It is also interesting to note that Basche (1964 b) already quarter of a century ago wrote about "current applications of pyrolytic boron nitride". Even today not much can be added to his article.

Table 4.1, presenting applications of h-BN based on different combinations of its properties, contains Basche's data with slight alterations.

One of the most often mentioned applications are vessels, especially crucibles for single crystal growth of semiconductor materials, in particular GaAs, and for vacuum evaporation/deposition of Al. Mostly free-standing BN pieces (usually prepared by deposition of BN on a graphite mandrel and then removed from it) have been used although BN-coated-graphite vessels can also be used.

Numerous other applications are related to electronics. These include B-dopant diffusion sources for semiconductors (Si), sodium diffusion barrier, semiconductor surface protection, thin film dielectric, insulators for electronic tubes.

Some papers mention other applications which are based on chemical stability of BN at elevated temperature: corrosion-resistant protective films which can be used in molten salt or corrosive gas environments, films for masking and passivation.

Applications such as die-wash material, lubricant, pressure-transmission medium, microwave/infrared windows and polarizers, furnace components, electrical feed-throughs have been mentioned.

Possibility of using chemical vapour infiltration of BN in order to obtain composites with different reinforcing fibres and different matrices has been dealt with only in a few papers, although this application seems to deserve more attention.

TABLE 4.1

Application of BN coatings

Applications ↓	Properties Desired ↗	High Purity	Chemically Reactive	Impervious	Oxidat. Resist.	Low Loss Tangent	High Breakdown Voltage & High Electrical Resistivity	Mechanical Strength at High Temperature	Thermal Anisotropy	Low Density
Furnace components					X			X		
Boats, trays, tank liners		X	X	X						
Crucibles		X	X	X	X					
Metal evaporator parts		X	X	X					X	
Electrical feed throughs				X	X		X	X		
Electrical insulators			X	X	X		X	X	X	
Nozzles			X	X	X			X	X	X
B-dopant diffusion source		X	X							
Coatings for graphite			X	X	X			X	X	
Heat shields				X	X			X	X	X
Microwave infrared windows		X		X		X	X	X	X	
Microwave infrared polarizers		X		X		X	X	X		
High temperature capacitors			X	X	X		X	X	X	
Mold linings		X	X	X				X	X	

5. CONCLUSION

By CVD and reactive PVD methods, the hexagonal (h-BN) and cubic (c-BN) crystal modifications of BN can be produced, corresponding to graphite and diamond, respectively. Energy of the gas or plasma constituents is apparently the main factor determining which crystal form will be produced.

In the conventional CVD methods, in which energy of the constituents is determined only by the temperature, only hexagonal form can be produced, the higher the temperature, the better ordered the deposit.

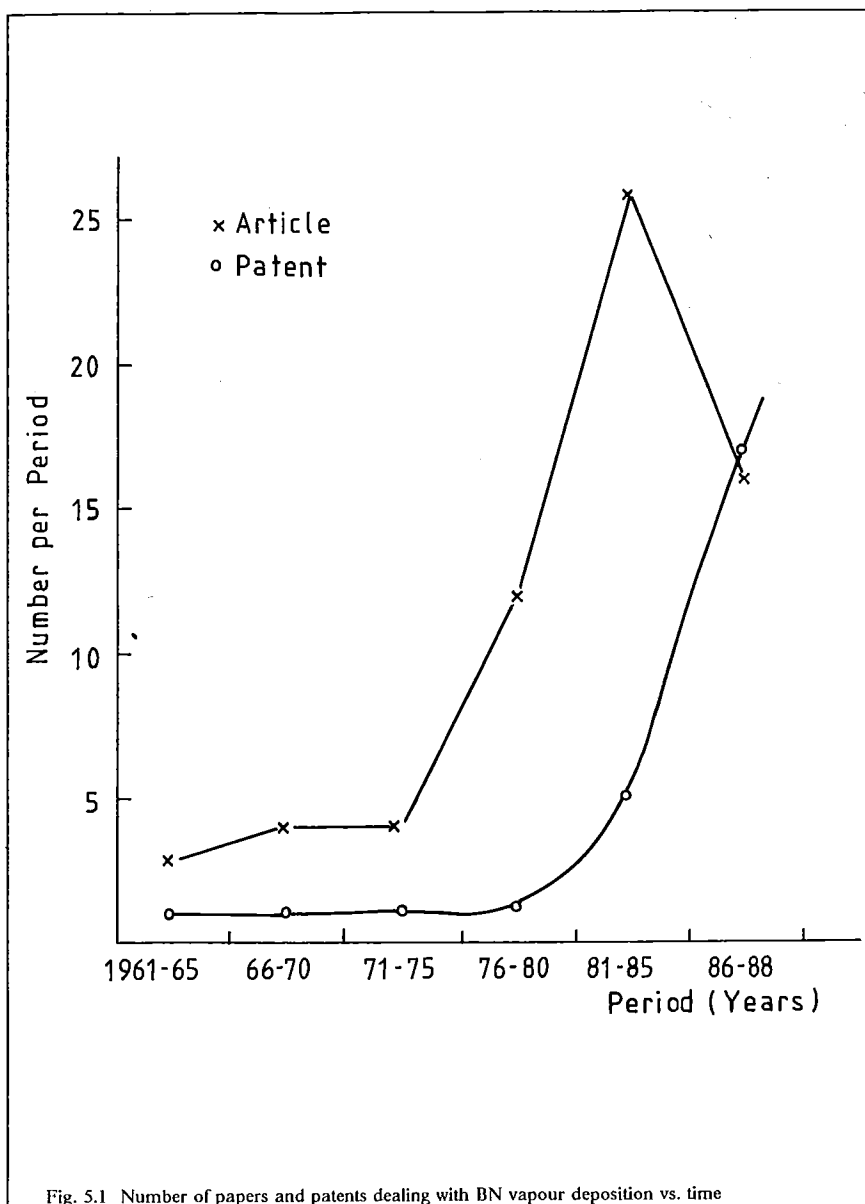
In the plasma-assisted CVD (PACVD) energy of the constituents is somewhat higher, but insufficient to produce cubic BN. However, ordered h-BN deposits can be produced at considerably lower temperatures than in the conventional CVD.

By the reactive PVD methods, in which energy of plasma constituents is up to 3-4 orders of magnitude higher, both h-BN and c-BN can be produced. However, in spite of the fact that the reactive PVD methods are more versatile, attention of researchers has been mostly directed to the CVD methods of BN preparation.

Concerning the number of papers and in particular number of patents, it is obvious that they have rapidly increased during the last several years (Fig. 5.1). Nevertheless, full use of potentialities of the vapour deposition methods for preparation of BN remains for the future.

The CVD methods, among which those using $\text{BCl}_3 + \text{NH}_3$ mixture (with or without other gases) have been predominantly treated, have advantages in offering high deposition rate (and, consequently, possibility of producing thick deposits), as well as high preferred orientation. They are used to produce either BN articles (such as BN crucibles) or components with BN coatings on different materials.

The BN deposits prepared by CVD generally have high preferred orientation of the hexagonal BN layers parallel to the substrate, high density, good adhesion to the substrate, impermeability to air, very low hardness (microhardness less than 0.62 GPa), very low friction, high electrical resistivity and extremely high dielectric strength. Because of high preferred orientation there is a high anisotropy of BN properties, in particular thermal conductivity ($0.63 \text{ W cm}^{-1} \text{ }^\circ\text{C}^{-1}$ parallel to the substrate surface, $0.01 - 0.03 \text{ W cm}^{-1} \text{ }^\circ\text{C}^{-1}$ perpendicular to it) and thermal expansion (coefficient of thermal expansion close to 0 parallel, $36.5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ perpendicular to the layers).



High electrical resistivity and good thermal conductivity is an unusual combination of characteristics, found only in BeO.

Applications of BN produced by CVD include BN or BN-coated-graphite vessels, in particular crucibles for semiconductor single crystal growth, B-dopant sources for semiconductors, insulators, surface protection layers with high corrosion resistance or improved oxidation resistance, masking, passivation, solid lubricant, heat shield etc.

The reactive PVD methods, in which conventional PVD devices are used to deposit BN layers by modified PVD methods where chemical reactions take place, are treated in a relatively small number of recent papers. They include mainly reactive sputtering from a BN cathode in N_2 gas, ion plating using reactive evaporation of boron in NH_3 or $N_2 + H_2$ gas mixture, or else H_3BO_3 , and ion-beam deposition of BN from borazine.

Main advantages of the reactive PVD methods are in using low substrate temperature (usually up to several hundred degrees °C) and possibility of producing cubic (and apparently wurtzitic) in addition to hexagonal BN.

The cubic BN layers are fine-grained, polycrystalline, thermally and chemically stable, very hard (microhardness up to 30 GPa), they have high friction, very high electrical resistivity and refractive index about 2.

Although these properties offer different possibilities of application, they have not yet been used.

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APPENDIX

Abbreviations and symbols used

α	NH ₃ /B-containing compound ratio
c-BN	Cubic BN
CTE	Coefficient of thermal expansion
CVD	Chemical vapour deposition
CVI	Chemical vapour infiltration
d	Density
DTA	Differential thermal analysis
D (X)	Flow rate of component X
E _B	Bennet electric field
E _g	Optical edge
FR	Flow rate
HB	Horizontal Bridgman
h-BN	Hexagonal BN
HCB	Hexachloroborazine
HT	Heat treatment
IR	Infrared
LEC	Liquid encapsulation Czochralski
LPCVD	Low-pressure chemical vapour deposition
MBE	Molecular beam epitaxy
MFCVD	Molecular flow chemical vapour deposition

MH	Microhardness
MWCVD	Microwave chemical vapour deposition
NTP	Normal temperature and pressure
P	Pressure
PACVD	Plasma-assisted chemical vapour deposition
PBN	Pyrolytic BN
PC	Pyrolytic carbon
PG	Pyrolytic graphite
P_o	Open porosity
PVD	Physical vapour deposition
P_X	Partial pressure of component X
R	Deposition rate
ρ	Electrical resistivity
r.f.	Radio frequency
σ	Breaking strength
T	Temperature
TCB	Trichloroborazine
T_d	Deposition temperature
TMB	Trimethoxyborazine
UV	Ultraviolet
VIS	Visible
XPS	X-ray photoelectron spectroscopy

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